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ELECTRIC OSMOSE.

[PRELIMINARY COMMUNICATION.]

BY J. C. W. FRAZER AND H. N. HOLMES.

In a series of experiments, made to determine the solution most efficient for removing the air from the pores of osmotic cells previous to the deposition of the semipermeable membrane,[1] the amount of water carried through the wall of the cell during the passage of a given current did not appear to be proportional to the resistance of the solutions of those electrolytes investigated, as deduced by Helmholtz.[2] The experiments given below were made to determine more accurately the relative osmose of a few of the salts of nitric acid at a concentration of 0.001 normal. Though the number of measurements is small and they are not as accurate as we hoped to get, it is thought best to publish the results now and continue the work at some future time.

Before presenting the results of the work a brief description will be given of the apparatus used. This is shown in the accompanying drawing.

The glass vessel *B* was made by cutting off the bottom of a half-liter bottle and inverting it as shown. The bottom of the bottle is used as a cover to protect the solution and the apparatus enclosed within. To secure a better joint between the two, a wide rubber band is slipped around the line of contact between the two parts of the bottle.

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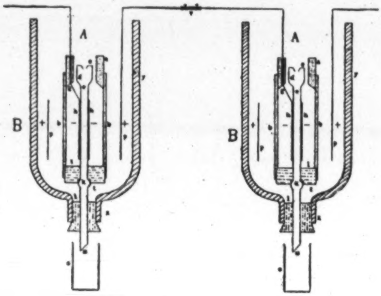
[1] THIS JOURNAL, **26**, 80.

[2] Wied. Ann., **7**, 351 (1879).



I *II*

The porous clay cell *b* is ground round for a distance of 15 mm. at each end and the soapstone washers, *a* and *i*, turned to fit accurately into these ground ends. In the center of *i* is a hole just large enough to allow the entrance of the drainage tube *e*. This tube is enlarged at *k* and the bulb so formed set firmly with shellac in the cavity *t*, after which the whole connection is painted with a solution of rubber in carbon bisulphide. Before setting the washers, *a* and *i*, in place their surfaces and the ground portions of the porous cell are painted with some of the same solution and when the rubber has been thoroughly hardened the joints at the two ends of the cell are perfectly tight and rigid. The purpose of the washer *a* and the enlarged upper end *d* of the glass tube is to limit the amount of liquid in the upper part of the cell and to give a large surface over which the liquid draining from the cell may flow, without diminishing the contents of the cell. To secure proper draining of the liquid from the cell at *d*, platinum discs with serrated edges were ground on the lathe the exact diameter of *d* and the interior of these caps was cut in the shape of teeth, meeting in the center, which are bent down so as to center the cap on *d*.

The platinum cathode *h* tightly clasps the glass tube and the wire leading to it passes through *g*. This hole is closed by the solution of rubber in carbon bisulphide. The anode *p* is a large platinum cylinder surrounding *b*.

The lower end of the glass tube *e* is ground to a sharp angle to facilitate the dropping of the liquid into the weighing bottle *o*.

The two parts, I. and II., of this apparatus are made as nearly alike as possible and are connected in series as shown in the illustration. The bottles rest upon a platform provided with two holes just large enough to admit their necks. This platform is simply a shelf in a box, so placed that the upper portions of the bottles project slightly through holes in the top of the box which is closed in front by a glass door, intended to exclude dust from the interior.

As jarring has considerable influence on the outflow of liquid at *d* the box is placed on an iron slab which is supported in sawdust.

To determine the point to which *B* must be filled previous to a measurement, it was filled with water to a point somewhat higher than *c* and allowed to stand for a long time until liquid ceased to drop from *m*, when a mark was made on *B* at the surface of the liquid. In operation *B* is filled to this mark and *b* to overflowing. After two minutes the weighing bottles are placed under *m* and a current of 36 volts passed for one minute through the two parts in series. After two minutes the overflow from each of the cells is weighed.

The object of having the apparatus duplicated is to use one of the parts, I., as a standard, keeping it always filled with 0.001 normal potassium nitrate solution so that the osmose of the solution in II. is expressed in terms of the osmose of that in I. Although the two parts, I. and II., were made as nearly alike as possible it is found ordinarily that when both are filled with the same solution different amounts of liquid will flow from the two. When both cells are filled with 0.001 normal solution of potassium nitrate the ratio of the amounts of liquid escaping from I. and II. enables one to correct for the differences in the two parts when some other electrolyte is put into II., thus allowing all measurements made in II. to be expressed in terms of the osmose of 0.001 normal potassium nitrate in I. It has been found that this cell ratio changes considerably when the apparatus is used too frequently or when the current is kept on for any length of time, due, probably, to the cell wall becoming electrified. For this reason the apparatus was not used frequently and the current kept on only one minute, and the cell ratio, with 0.001 normal potassium nitrate in both, was frequently redetermined.

The following tables give the relative osmose of the various electrolytes indicated to that of potassium nitrate which is assumed arbitrarily to be 100. All the solutions were made 0.001 normal and the water which was used had a conductivity of about 1.5×10^{-6} at 25°.

Table I.—Sodium Nitrate.[1]

	147.9	147.2	150.5	148.8
	147.2	142.7	151.8	150.7
	148.4	148.8	. . .	149.1
Mean,	147.8	146.2	151.1	149.5

Table II.—Ammonium Nitrate.

	103.5	103.2	102.7
	102.9	102.5	103.0
	103.7	102.3	102.7
Mean,	103.4	102.6	102.8

Table III.—Lithium Nitrate.

	184.3
	182.8
	183.7
	179.5
Mean,	182.6

Table IV.—Caesium Nitrate.

	97.6
	96.9
	95.3
	. .
Mean,	96.6

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[1] These measurements of 0.001 sodium nitrate were made in an apparatus of different form which has not been shown to be as reliable as the one described above, but the results agree better among themselves.

Table V.—Rubidium Nitrate.

97.0	97.4	97.4	96.9
96.8	97.2	98.2	95.7
		Mean,	97.1

Table VI.—Barium Nitrate.

	61.7
	59.6
	53.9
	..
Mean,	58.4

Table VII.—Calcium Nitrate.

	62.4
	63.6
	67.8
	65.4
Mean,	64.8

Table VIII.—Strontium Nitrate.

	61.1
	58.0
	65.0
Mean,	61.3

Lack of time prevented a quantitative study of the osmose of acids and bases in a manner similar to the above work on the nitrates. But when cell I. was filled with 0.001 normal solution of potassium nitrate and cell II. with 0.001 normal nitric acid and the determination made just as had been done in one of the experiments given above it was found that the surface of the liquid inside the cell *b* fell. A second determination was made of nitric acid and the electrodes in part II. reversed. Liquid now dropped from both outlet tubes. In this and a number of similar experiments the amount of negative osmose from cell II. was about 14 per cent of that from cell I. Acetic acid (0.001 normal) was next put into cell II. and the negative osmose was much greater. The amount of liquid coming from cell II. was 1.28 times greater than that from cell I.

In the table below we have brought together the means of all the measurements made, together with the relative specific resistances of the solutions used. The values for the resistance are taken from Kohlrausch and Holborn's

"Leitvermögen der Elektrolyte" and for the sake of comparison are so calculated as to make the resistance of 0.001 normal potassium nitrate solution equal to 100, as shown in column IV.

I.	II. Osmose.	III. Calculated osmose.	IV. Relative specific resistance.
KNO_3	100.0	100.0	100.0
$NaNO_3$	149.1	148.4	120.7
NH_4NO_3	102.9	101.6	98.7
$LiNO_3$	182.6	187.3	139.6
$CsNO_3$	96.6	95.2	...
$RbNO_3$	96.9	95.2	...
$\frac{1}{2}Ba(NO_3)_2$	58.4	61.0	108.9
$\frac{1}{2}Sr(NO_3)_2$	64.8	66.6	113.8
$\frac{1}{2}Ca(NO_3)_2$	61.3	65.1	114.3

It is seen from column III. of this table that the solutions studied follow rather closely the rule, which has been previously stated,[1] that the osmose of the nitrates of the alkalies and alkaline earths varies inversely as the velocity of the cation divided by its valence. But the osmose does not seem to be proportional to the specific resistances of the solutions, as shown by comparing the values in column II. and those in column IV.

The rule which is tentatively advanced is that the amount of osmose of various salts with a common anion varies approximately inversely as the velocity of the cation divided by its valence.

There may be some connection between this phenomenon and the results obtained by Kohlrausch[2] and others in their work on the hydration of the ions.

Viewed in the light of this hypothesis of Kohlrausch the above experiments on the osmose of 0.001 normal nitric and acetic acids have additional interest. Here we have the fastest moving cation and two anions of very different velocities. As the flow of liquid is opposite to the direction of the current there can be no relation between the osmose and the resistances of the solutions. Besides, this negative flow is much greater in the case of acetic acid where the resistance is greater than with nitric acid.

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[1] This Journal, **36**, 28.

[2] P. Roy. Soc., **71**, 348.

IMPROVEMENTS IN MANOMETERS FOR THE MEASUREMENT OF OSMOTIC PRESSURE.[1]

By H. N. Morse and B. F. Lovelace.

We became convinced, in the course of our measurements during the past year, that the temperature coefficient of osmotic pressure could not be satisfactorily determined without a very considerable improvement in the method. The pressures which had been observed at 20° were so nearly equal to those found at 0° and 5°, and all of these differed so little from those we were finding at 10° and 15°, that the differences appeared to be covered by the possible errors of the work. The present year has therefore been largely spent in improving the method in every way which could contribute to the precision of the measurements.

The largest sources of error and uncertainty were connected with the construction of the cell and the manner of closing and opening it, and these were eliminated, first of all, by radical changes in the form of the cell and in its manometer attachments. The nature of the errors inherent in the old form of cell and the measures which were taken to correct them have been described in a former paper.[2]

Errors due to fluctuating temperature in the bath (*thermometer effects*) probably come next in the order of importance, and these were corrected by a system of automatic bath regulation which will be described in a later paper.

The present paper deals with improvements in the manometric portion of the work.

It is clear that, though a constant pressure which a solution is exerting may be, and often is, below the true maximum pressure, or, under certain conditions, above it, the *correct determination* of that pressure depends principally on the reliability of the manometer, and that, on this account, it is impossible to give too much attention to the calibration, comparison, and testing of this instrument. Idiosyncrasies of the readers can be—and, in our practice, are—eliminated by the "check" system, according to which important readings at the telescope (and also at the polariscope) are made independently by two or more individuals.

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[1] The work upon osmotic pressure which is in progress in this laboratory is aided by grants from the Carnegie Institution. The earlier papers upon the subject will be found in This Journal, **26**, 80; **28**, 1; **29**, 173; **32**, 93; **34**, 1; **36**, 1 and 39; **37**, 324, 425, and 558; **38**, 175; **39**, 667; **40**, 1, 194, and 266.

[2] This Journal, **40**, 266.

The gas space in our manometers under atmospheric pressure is from 400 to 500 millimeters in length; hence, under the highest osmotic pressures (25-26 atmospheres) it may not have a length of more than 15 and a fraction millimeters, and the correction for meniscus alone may amount to more than 0.3 atmosphere. These facts will suffice to emphasize the care required in calibrating the tube, especially the upper end of it, and at the same time to explain the necessity of permanently filling with mercury all that portion of the top whose capacity has been affected by the operation of closing the manometer. Formerly, the introduction of this mercury was attended with considerable difficulties, which, however, have been overcome in the later method of filling the instruments. With equal care in calibration, a higher degree of accuracy could be secured by making the manometers longer, but it is not practicable to increase their length to any great extent, owing to the difficulty of obtaining long tubes which are sufficiently straight. Moreover, long tubes are much more likely to be broken by handling, and are less easily provided for in the bath.

The internal diameter of the manometer has remained from the first about 0.5 mm. Some advantage would be gained by using tubes of larger bore—especially in the greater distinctness of the meniscus—but whenever this has been tried, minute globules have become detached from the upper, stationary column of mercury, and it is often impossible to remove these from the glass and incorporate them with the mercury below. The same objection to large bore does not hold in the case of the *standard manometer* which is used only for testing and verifying the others, and is not, therefore, subjected to so much rough usage as those which are put up with the cells. The standard manometer in use has an internal diameter of 2 mm.

Originally, the manometers were filled with dry air, but it was soon discovered that the volume of the enclosed gas gradually diminished, the decrease in some instances amounting to more than one per cent. It was assumed that the loss in volume must be due to impurities in the mercury which were attacked by the oxygen, though great pains had been taken in the purification of the mercury, and none of the appearances characteristic of the impure metal could be detected either on the mercury itself or on the glass tubes. The manometers were therefore filled with nitrogen instead of air. But it must not be overlooked that there is another possible explanation of the apparent diminution in gas volume, namely, a permanent stretching of the manometer under pressure, and any complete system of manometer control must include a provision for determining whether, and to what extent, a manometer is stretched—either temporarily or permanently—by the pressure to which it is subjected.

In determining capillary depression and the volume of the enclosed gas, and also in calibrating, the manometer must be joined to another glass tube, between which and the former there is free communication, and any lack of rigidity in the walls of the communicating channel gives rise to difficulties which are often very aggravating to the experimenter. But when manometers are to be compared with each other or with a standard, and when the question of stretching is to be investigated, absolute rigidity in this part of the apparatus is indispensable. The earlier forms of apparatus used by us were all imperfect in that they did not permit effective comparisons at pressures above 2 atmospheres. The apparatus which was devised during the past year, however, enables us to carry the investigation of the manometers up to pressures of 300 atmospheres. It is shown in section in Figure 1. It consists of a rectangular steel block which has been bored from end to end in the horizontal direction (*a*, Figure

1). Meeting the horizontal hole are two vertical holes, *b* and *c*. The latter serve as receptacles for two manometers which are to be compared or tested, one of which may be

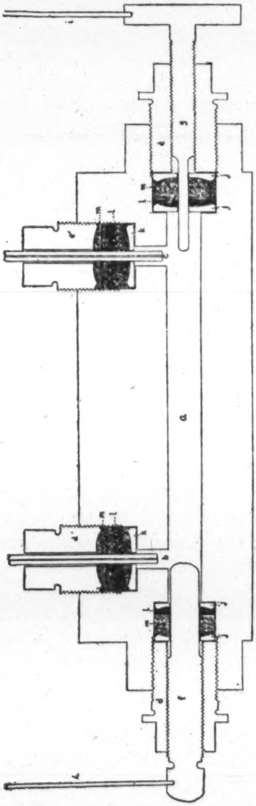

FIG 1

the standard manometer; or one may be occupied by a manometer and the other by a straight open tube, as in calibrating or in determining capillary depression, etc. At the ends of the block, the horizontal hole is bored out to a larger diameter and the wider parts are threaded to receive the steel plugs *d* and *e*, which hold the packing in place. The packing plugs are in turn bored and threaded to receive the plungers *f* and *g*, by means of which the pressure is regulated. The two plungers differ only in respect to size. One has nearly the diameter of the hole *a*, and serves for coarse adjustments; while the other is small, and is employed to effect slight changes in pressure. Both are operated by levers shown at *h* and *i*. The packing plugs in the vertical holes, *d′* and *e′*, are bored but not threaded, and their lower ends are concave in form.

The packing through which the plungers pass lies between two steel disks, *jj*, both of which are concave on the side facing the packing, except near the circumference, where they are cut back as shown in the figure. The purpose of the concave form of the disks is obviously to bring increased lateral pressure upon the plunger and thus prevent the leakage of mercury. A similar effect is produced in the opposite direction at the circumference by cutting back the edges of the disks. The arrangement in the vertical holes is similar. Here the packing also lies between two concave surfaces, one of which is furnished by the steel disk *k*, and the other by the plug *d′* or *e′*. It will be seen that any desired amount of pressure may be brought upon the packing by turning the plugs *d* and *e*.

The packing consists of rubber (*l*, *l*, *l*, and *l*) and leather (*m*, *m*, *m*, and *m*). The rubber is placed next the mercury in all packed regions in order to cleanse the advancing plungers or manometer tubes from any grease which may have been derived from the leather. If proper packing material is selected, and the packing plugs are screwed down tightly upon it, the pressure may be raised to 300 atmospheres without leakage of mercury or displacement of the glass tubes.

When a manometer tube is to be calibrated, it is drawn out and bent over at the upper end, as shown in Figure 2. The lower part—including the two bulbs and the horizontal portion—is filled with mercury, and the instrument is then secured in its place in the steel block. In order to introduce the required calibrating thread, one of the plungers is turned until the tube, except a small space at the top, is filled with mercury. A small cup of mercury is then brought up to the open end, and the plunger is turned in the reverse direction until the required amount of metal has been introduced. This leaves the calibrating thread separated from the main column of mercury by an air space, as shown at *a* in Fig. 2. It is evident that both the air space and mercury thread can

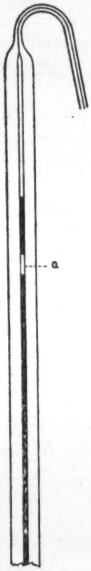

FIG 2

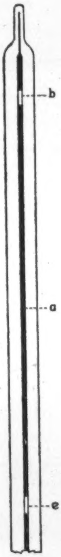

FIG 3

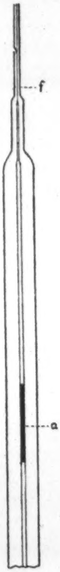

FIG 5

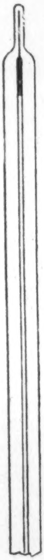

FIG 6

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easily be made of any desired length. The latter usually has a length of 12 to 15 millimeters.

By turning the plunger, the calibrating thread is brought down the manometer until its lower end reaches the line etched upon the glass which indicates the point at which the calibration is to begin, when the meniscus at both ends is developed by tapping the tube. The length of the space filled by the mercury thread is determined by means of the telescope and the standard meter. The thread is then raised until the bottom of the lower meniscus occupies quite exactly the former position of the top of the upper one, when the readings are repeated. Each movement of the mercury must, of course, be followed by a tapping of the tube until the form and the position of the meniscus become fixed; hence the exact setting of the thread requires some time, and always the coöperation of two persons, one of whom operates the plungers and taps the tube under the direction of the other, who is stationed at the telescope.

The calibrating thread is thus set end to end and its length determined, until the top of the tube is reached, when it is returned to the starting point and the operation is repeated. If the two records are found to be in accord at all points, the calibration is regarded as finished. If, on the other hand, discrepancies appear, the work is repeated until the different series of readings are harmonious throughout. It is then necessary only to reduce the readings and to plot a curve of corrections for the manometer.

The second step in the preparation of the manometer is to determine the correction for meniscus. This is done in the following manner: The calibrating thread is run out of the manometer and weighed and its volume is calculated. A long thread of mercury, which exactly fills the calibrated portion of the tube, is then introduced. This is also run out and weighed and its volume calculated. The difference between the volume of the long thread and that of the short one, multiplied by the number of settings, is clearly equal to all spaces which were not filled by the mercury when the calibrating thread was set end to end up the tube, and the correction for a double meniscus will be found by dividing the total volume of this waste space by the number of settings less one.

The plan which is employed in investigating the stretching of manometers is most conveniently explained at this point, though the preparation of the tubes for that purpose cannot be understood until the method of filling the manometers has been described. Fig. 3 represents a calibrated tube which is to be tested. It will be noted that a long thread of mercury (*a*) is cut off from the mercury above and below by short spaces filled with air (*b* and *c*), or, better, with nitrogen. A tube, prepared as shown in the figure, is placed in the steel block, and the contents are subjected to any required pressure. It is obvious that, if stretching occurs, the imprisoned thread of mercury will shorten, and that the amount of the stretching can be determined, since all parts of the tube have been accurately calibrated. Moreover, it can be ascertained whether any observed stretching is temporary or permanent; for, if it is temporary, the thread will recover its original length when the pressure is removed. A permanent stretching of the manometer can also be detected, and the amount of it ascertained by redetermining, under a known pressure, the volume of the enclosed nitrogen.

The testing of a manometer by comparing it with the standard instrument is a simple operation which is employed to detect and correct errors of any kind, whether they are due to faulty calibration or a permanent stretching of the glass, or, possibly, to an incorrect previous determination of the volume of nitrogen. The standard manometer is made from heavier tubing, and has a larger bore than the instruments which are used with the cells, and every practicable measure is employed to insure its correctness. When a comparison is to be made, the standard is fixed in one of the receptacles of the steel block, and the manometer to be tested in the other. A series of equal pressures are brought upon the gas volumes of the two instruments, and the values of these, as determined by the standard, are compared with the pressures which are calculated from the calibration data of the manometer under examination.

The comparison of any one manometer with another is precisely like its comparison with the standard. The occasion for such a comparison arises whenever the osmotic pressures which are found in the course of duplicate determinations appear to differ more widely than the other known sources of error in the method will justify.

The method of determining the capillary depression of a manometer presents no novel features. The open manometer is fixed in one of the receptacles of the steel block, and a tube with a broader upper part in the other, and the mercury is forced up until it enters the wider portion of the second tube. The difference in the level of the mercury in the two tubes is the capillary depression of the manometer. Since all of our manometers have about the same bore, *i. e.*, 0.5 mm., the correction for capillary depression is about constant, and varies but little from 0.02 atmosphere.

The nitrogen which is used to fill the manometers is obtained by passing air first through an alkaline solution of pyrogallol, and then, in the order named, over heated copper oxide, heated copper, heated copper oxide, calcium chloride, fused potassium hydroxide, and resublimed phosphorus pentoxide. The glass tubes containing the dry reagents are all connected with each other and with the receptacle for the nitrogen by fusing the ends together.

We have had occasion to answer many inquiries regarding our method of filling and closing manometers, which suggests that a somewhat detailed account of the procedure may be of use to others who are engaged in work with these instruments.

The arrangement of apparatus which is employed for the purpose is shown in Fig. 4. *A* is the reservoir for nitrogen; *B* is the calibrated manometer which is to be filled and closed; and *C* is an arrangement for filling and emptying the manometer. *B* is joined to *A*, at *d*, by fusing together the ends of the glass tubes and to *C*, at *e*, by means of rubber tubing. The mercury in *C* is separated from that in the manometer by the air which nearly fills the wide tube below *e*. In this way, the mercury in *C*, which may be impure from its contact

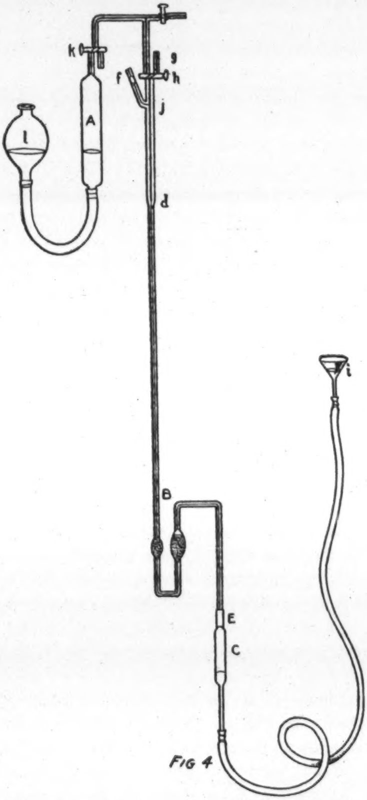

FIG 4

with rubber tubing, is prevented from ever entering the manometer and contaminating the very pure mercury with which that instrument is filled. This air also plays an important rôle when the manometer is closed.

Before joining the manometer *B* to *A* and *C*, its lower end is immersed in pure mercury and, with the instrument in an inclined position, gentle suction is applied at the other end until the two bulbs are filled with mercury. The introduction of the mercury in such a manner that the column between the two bulbs remains unbroken is an operation of some difficulty at first, but it is readily accomplished after a little practice. It is hardly necessary to state that the mercury which is used in manometers should never be allowed to come in contact with rubber.

The side tube *f* is closed with a short piece of rubber tubing and a screw pinchcock, and is connected with a drying apparatus. When the manometer is sealed to *A* at *d*, there is danger that some moisture from the flame will be deposited on the inside of the tube. To remove this, the tube is kept warm at *d*, while dried air is repeatedly introduced through *f* and expelled through *g*.

The next step is to fill the manometer with nitrogen from the reservoir *A*. The reservoir *i* is raised, and the air in the manometer is expelled through *g*, until the mercury column reaches the point *j*, when the stopcock *h* is closed and a small quantity of mercury is introduced into the side tube *f*. This is the mercury which is afterwards to occupy the upper end of the closed manometer. The rubber tube upon the end of *f* is now tightly closed, and the air remaining between *j* and the stopcock *h* is expelled through *g*, care being taken not to allow the mercury quite to reach the stopcock, lest it should be contaminated by some of the lubricating material on the latter. By turning the stopcocks *h* and *k*, and lowering *i* or raising *l*, the manometer is filled with nitrogen from *A*. This is wasted through *g*, and the manometer is again filled from *A*; and the operation of filling and emptying is repeated as often as may be thought necessary.

When the manometer has been filled for the last time, the reservoir *i* is adjusted to the right level and the gas is placed under very slightly increased pressure by raising the reservoir *l*. The stopcock *h* is opened to the air and instantly closed. This leaves the nitrogen in the manometer under a pressure equal to that of the atmosphere.

By gently pinching the rubber tube which closes *f*, a little mercury is forced out of the side tube into the vertical one between *j* and *d*; and by continuous tapping the small globules which separate at *j* from the thread in *f* are brought down the tube and made to collect above *d* in a continuous column. The mercury thus transferred from the side tube *f* to *d* does not enter the manometer, owing to the smallness of its bore.

The reservoir *i* is now lowered until all the mercury collected above *d* has been drawn into the manometer to a convenient distance below that point, when the glass at *d* is softened in the blowpipe flame, and the manometer is detached, but in such a manner as to leave both tubes sealed.

The glass at the closed end of the detached manometer is again softened in the flame, and the top of the tube is drawn out as shown in Fig. 5, that is, into a moderately wide capillary with thick walls below, and an *exceedingly* fine capillary above. After the tube has cooled down sufficiently, the column of mercury, *a*, Fig. 5, is forced upwards until it fills both capillaries, when the smaller one is fused off at *b* (under slightly diminished internal pressure), leaving the top of the manometer as shown in Fig. 6.

Great care is required in closing the manometer not to convert any considerable amount of the metal into vapor, and to heat the glass so uniformly that the vapor which is necessarily formed cannot recondense until the operation of closing is finished. Otherwise, the violent agitation of the mercury, due to rapid vaporization and condensation, is apt to shatter the tube.

Having filled and closed the calibrated manometer, the volume of the nitrogen, under standard conditions of temperature and pressure, must be ascertained. For this purpose, the instrument is placed in one of the receptacles of the steel block, and a long straight tube of equal bore in the other. The volume of the nitrogen is then found under several known light pressures, and its volume under the standard pressure and at the standard temperature is calculated.

It remains only to compare the instrument with the standard manometer, but that operation has already been sufficiently described in connection with the uses of the steel block.

JOHNS HOPKINS UNIVERSITY,
June 1, 1908.

[Contributions from the Sheffield Laboratory of Yale University.]

CLIX.—RESEARCHES ON HALOGEN AMINO ACIDS: 3,5-DIBROMPHENYLALANINE.

[FOURTH PAPER.]

BY HENRY L. WHEELER AND SAMUEL H. CLAPP.

This paper may be considered as a preliminary contribution to the study of halogen substitution products of phenylalanine, or phenylaminopropionic acid. There appears to be no description of such substances in the literature of the acid. It is expected that a knowledge of the properties of these halogen derivatives, their stability toward reagents, etc., will prove of service in deciding the question of the position of halogens in protein substances.

The interesting and important work of Mörner[1] has shown that not only iodine[2] but also bromine and chlorine are widely met with in the skeletal tissue of the lower marine animals. Hundeshagen[3] previously found that all three halogens occur in organic combination in sponges, presumably, he states, in aliphatic amino acids or in tyrosine.

On account of Millon's test giving a negative result, Hofmeister[4] was the first to suggest that iodine enters the tyrosine molecule in iodalbumin. Blum and Vaubel[5] also expressed the view that iodine is combined in the tyrosine nucleus; that it does not replace the hydroxyl group but that, instead, it substitutes in the adjacent positions to this group. In the first paper of this series Wheeler and Jamieson[1] showed that Drechsel's iodgorgoic acid,[2] which is the only crystalline halogen amino acid that has yet been obtained from protein substances,[3] is in fact diiodtyrosine and not, as Drechsel supposed, iodaminobutyric acid.

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[1] Z. physiol. Chem., **51**, 33 (1907); **55**, 77 (1908).

[2] See also Harnach: *Ibid.*, **24**, 412 (1898); Mendel: Am. J. Physiol., **4**, 243 (1901); Cook: *Ibid.*, **12**, 95 (1905).

[3] Z. angew. Chem., **1895**, 475.

[4] Z. physiol. Chem., **24**, 159 (1898).

[5] J. prakt. Chem., **57**, 365 (1898).

Nürnberg[4] has recently published results, obtained by heating iodthyrin with water under pressure, which indicate that iodine substitutes in both the tyrosine and tryptophane molecules[5] in this substance.

On the other hand Oswald[6] has brought forward strong arguments to show that it is neither tyrosine nor tryptophane that exclusively contains the halogen. He suggested, however, that iodine enters exclusively or for the most part the aromatic groups and he concluded from his results and those of Pick,[7] in the case of the iodized proto- and heteroalbumoses, that phenylalanine is substituted by the halogen.

Several syntheses of phenylalanine have been devised, among which, perhaps, the two most practicable are the synthesis of Emil Fischer[8] and that of S. P. L. Sörensen.[9]

The first step in Fischer's synthesis is the preparation of benzylmalonic acid. It has been frequently observed when a benzyl halide containing negative groups is allowed to act on the monosodium salt of malonic ester that a dibenzyl- and not exclusively a monobenzylmalonic ester is formed. For example ortho- or paranitrobenzyl chloride reacts with the monosodium ethyl malonate to give, as chief product, a di(nitrobenzyl) malonic ester,[10] $(NO_2C_6H_4CH_2)_2C(CO_2C_2H_5)_2$.

In the present work we first observed that 3,5-dibrombenzyl bromide reacts in a similar manner and that di(3,5-dibrom-

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[1] THIS JOURNAL, **33**, 365; also Third Paper, *Ibid.*, **38** 356 (1907).

[2] Z. Biol., **33**, 90 (1896).

[3] See also Henze: Z. physiol. Chem., **38**, 360, and **51**, 64 (1907).

[4] Beitr. chem. Physiol. u. Path., **10**, 125 (1907).

[5] Compare Blum: Z. physiol. Chem., **24**, 159; Rhode: *Ibid.*, **44**, 161 (1905).

[6] Beitr. chem. Physiol. u. Path., **3**, 391, 413 (1903).

[7] Z. physiol. Chem., **24**, 246 (1898).

[8] Ber. d. chem. Ges., **37**, 3062.

[9] Compt. rend. Trav. Lab. Carlsberg, **6**, 6 (1902); Centrabl., **1903**, II., 33; Z. physiol. Chem., **44**, 448 (1905).

[10] Lellmann and Schleich: Ber. d. chem. Ges., **20**, 434 (1887).

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benzyl)malonic ester, $(Br_2C_6H_3CH_2)_2C(CO_2C_2H_5)_2$, results as the chief product.[1]

It was then found that the elegant synthesis of Sörensen, which has been so successful in other cases, could also be used with the above benzyl bromide and that it gave an excellent yield of the desired dibromphenylalanine.

The new 3,5-dibrombenzyl bromide was prepared by adding bromine to 3,5-dibromtoluene at 170°–180°. The product thus obtained differed decidedly from the two possible isomeric tribromtoluenes;[2] the bromination had therefore taken place in the methyl group.

3,5-Dibrombenzyl bromide and the sodium salt of phthalimidomalonic ester reacted at 140°–150° as follows:

$$Br_2C_6H_3CH_2Br + NaC(CO_2C_2H_5)_2N(CO)_2C_6H_4 = Br_2C_6H_3CH_2C(CO_2C_2H_5)_2N(CO)_2C_6H_4 + NaBr.$$

I.

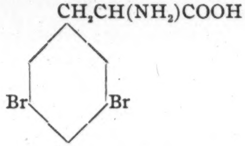
The 3,5-dibrombenzylphthalimidomalonic ester, I., when warmed with alkali and the solution acidified, gave the substituted malonic acid, II., which readily lost carbon dioxide, forming the phthalamic acid derivative, III. When this was heated with strong hydrochloric acid the phthalyl group was removed as phthalic acid and, on evaporating and treating the mixture with ammonia, 3,5-dibromphenylalanine, IV., was obtained. The yields, after the preparation of the benzyl bromide, were excellent.

$$Br_2C_6H_3CH_2C(COOH)_2NHCOC_6H_4COOH$$

II.

$$Br_2C_6H_3CH_2CH(COOH)NHCOC_6H_4COOH$$

III.



IV.

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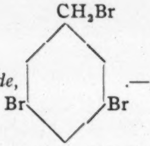
[1] The 3,5-dibrom compound is perhaps not the most probable naturally occurring bromine derivative of phenylalanine. We selected it as the first derivative for study, however, with the intention of eventually employing it in settling the structure of the halogen tyrosines.

[2] Nevile and Winther: Ber. d. chem. Ges., **13**, 974 (1880).

EXPERIMENTAL PART.



3,5-Dibrombenzyl Bromide, .—3,5-Dibromtoluidine was prepared according to the directions of Klages and Liecke.[1] The amino group was then removed in the manner described by Jackson[2] and others in the case of tribromaniline.

Forty-two grams of dibromtoluene were heated in an oil bath at 170°–180° and to this one molecular proportion of bromine was added drop by drop. The contents of the flask were then cooled and the crystalline mass was extracted with hot 95 per cent alcohol. The substance remaining insoluble was nearly pure dibrombenzyl bromide since, after recrystallizing once from 95 per cent alcohol, it melted constantly at 95°–96°.

In another experiment 61 grams of 3,5-dibromtoluene at 175° and 42 grams of bromine, after extracting and crystallizing the product once from alcohol, gave a yield amounting to 45 per cent of the calculated.

3,5-Dibrombenzyl bromide crystallizes from 95 per cent alcohol in prisms, or long needles forming a feltlike mass. It is difficultly soluble in cold alcohol. It appears to be slightly volatile in the vapor of alcohol and it violently attacks the eyes. It was observed to boil unaltered at 173° at 19 mm. pressure and at 169° at 15 mm. pressure.

A determination of the replaceable bromine, of the side chain, was made by heating the substance in an alcoholic solution of sodium ethylate, evaporating to dryness, acidifying with nitric acid, and precipitating in the usual manner.

1.0257 gram of substance gave 0.5924 gram of AgBr.

0.3271 gram of substance gave 0.3104 gram of CO_2 and 0.0516 gram of H_2O.

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[1] J. prakt. Chem. [2], **61**, 326 (1900).

[2] THIS JOURNAL, **12**, 167 (1890); **14**, 335 (1892).

	Calculated for $C_7H_5Br_3$.	Found.
Br	24.32	24.58
C	25.53	25.86
H	1.51	1.74

The mother liquors from the purification of the benzyl bromide gave a substance melting at 43°, probably 2,3,5-tribromtoluene.

Ethyl Phthalimidomalonate, $HC(CO_2C_2H_5)_2N(CO)_2C_6H_4$.—This was prepared according to Sörensen's[1] directions.

3,5-Dibrombenzylphthalimidomalonic Ethyl Ester, $Br_2C_6H_3CH_2C(CO_2C_2H_5)_2N(CO)_2C_6H_4$.—Twenty-seven grams of phthalimidomalonic ester were quickly added to a solution of the required amount of sodium ethylate in 300 cc. of dry alcohol, kept at about 40°. A clear, orange colored solution resulted, from which, on warming, the sodium salt separated as a yellow crystalline precipitate. The alcohol was then removed by distillation under reduced pressure, the last traces being removed finally by heating in an oil bath at 130° for three hours. Twenty-nine grams of dibrombenzyl bromide were then added (equal molecular proportions) and the mixture was heated at 140°–150° for 14 hours. At the end of the reaction the contents of the flask formed an oily mass, which, on cooling, hardened to a yellow crystalline cake.

The reaction product was then dissolved in boiling alcohol, and on cooling separated in stout prisms. The yield of pure substance was 39 grams, which is 80 per cent of the calculated.

As pointed out by Sörensen in other cases, the success of this synthesis depends largely on having the sodium salt of phthalimidomalonic ester free from water and alcohol. The ester should be very quickly mixed with the alcoholic sodium ethylate, as otherwise the salt frequently begins to separate before the addition of phthalimidomalonic ester is complete and the contents of the flask solidify to a gelatinous mass of the sodium salt, enclosing large quantities of unaltered ester. In one experiment in which the salt was heated with the benzyl bromide at 145° for only 3 hours, using 40.5 grams of phthalimidomalonic ester, the yield of crude product was 64 per cent of the calculated.

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[1] *Loc. cit.*, or see Centrabl., **1903**, II., 33.

3,5-Dibrombenzylphthalimidomalonic ethyl ester is insoluble in water, readily soluble in hot, and difficultly soluble in cold alcohol. It forms prisms and plates, often in aggregates. It melts at 144°–145° to a clear oil.

I. 0.2618 gram of substance gave 6.6 cc. moist N at 20° and 752 mm. pressure.
II. 0.0927 gram of substance required 1.8 cc. N/10 HCl.
III. 0.1574 gram of substance gave 0.1064 gram AgBr.
IV. 0.2249 gram of substance gave 0.1541 gram AgBr.

	Calculated for $C_{22}H_{19}O_6NBr_2$.	Found. I.	II.	III.	IV.
N	2.53	2.85	2.72	....	....
Br	28.92	....	....	28.77	29.18

3,5-Dibrombenzylmalonicacidphthalamic Acid, $Br_2C_6H_3CH_2C(COOH)_2NHCOC_6H_4COOH$.—For saponification, 30 grams of the above ester, finely pulverized, were suspended in 100 cc. of 5 N sodium hydroxide solution and warmed on the water bath for 6 hours. At the end of this time, the sodium salt had separated as a bulky mass difficultly soluble in the excess of alkali. Water was then added and, after filtering from a trace of unaltered ester, the free acid was precipitated by adding hydrochloric acid in slight excess to the cold solution.

The precipitate, which at first was oily, solidified on standing to a snow-white mass of prismatic crystals. A portion which remained floating on the supernatant liquid was removed and found to consist of well-developed prismatic forms, which began to lose carbon dioxide at about 110° with effervescence and in consequence possessed no sharp decomposition point. Nitrogen determinations agreed with the calculated values for a malonic acid derivative:

I. 0.4192 gram substance gave 10.2 cc. of moist N at 20° and 753.5 mm. pressure.
II. 0.2318 gram substance required 4.7 cc. N/10 HCl.

	Calculated for $C_{18}H_{13}O_7NBr_2$.	Found. I.	II.
N	2.71	2.76	2.84

Owing to the ease with which this substance loses carbon dioxide it could not be recrystallized. On boiling with water it readily loses carbon dioxide and is converted into:

3,5-Dibrombenzylaceticacidphthalamic Acid, $Br_2C_6H_3CH_2CH(COOH)NHCOC_6H_4COOH$.—This compound is the chief product obtained when the sodium salt above mentioned is acidified with hydrochloric acid without cooling. The yield is nearly quantitative. It was recrystallized by dissolving in warm alcohol, in which it is very soluble, and cautiously adding water to faint turbidity. It separated in dense clusters of minute prisms which melted to an oil, with considerable effervescence, at about 174°. It is almost insoluble in cold water.

I. 0.3530 gram substance gave 9.7 cc. moist N at 19° and 762 mm. pressure.

II. 0.1289 gram substance required 2.9 cc. N/10 HCl.

III. 0.1213 gram substance required 2.75 cc. N/10 HCl.

	Calculated for $C_{17}H_{13}O_5NBr_2$.	Found. I.	II.	III.
N	2.97	3.16	3.14	3.17

3,5-Dibromphenylalanine, $Br_2C_6H_3CH_2CH(NH_2)COOH$.—The foregoing derivative of phthalamic acid is readily saponified by boiling hydrochloric acid. Eighteen and one-half grams were finely pulverized and boiled with 20 per cent hydrochloric acid with a return condenser. Without apparently going into solution the powder was replaced by clusters of prismatic crystals and after continuing the boiling for 3 hours the saponification was complete. The solution was then concentrated to a volume of about 100 cc. and an equal volume of hydrochloric acid of specific gravity 1.19 was added. After standing some time the precipitate was filtered off and found to consist of a mixture of phthalic acid and the hydrochloride of 3,5-dibromphenylalanine.

In order to separate these acids the mass was dissolved in ammonia and the solution concentrated, whereupon the free dibromphenylalanine separated as a bulky mass, while the phthalic acid remained in solution. The yield corresponded to 92 per cent of the calculated. The acid was recrystallized from water for analysis.

I. 0.2872 gram substance gave 0.3551 gram CO_2 and 0.0829 gram H_2O.

II. 0.1854 gram substance gave 7.2 cc. moist N at 770 mm. and 16.5°.

III. 0.2565 gram substance required 8.05 cc. N/10 HCl.

IV. 0.2043 gram substance required 6.6 cc. N/10 HCl.

V. 0.1748 gram substance gave 0.2023 gram AgBr.

	Calculated for			Found.		
	$C_9H_9O_2NBr_2$.	I.	II.	III.	IV.	V.
C	33.44	33.71	....	....	....	....
H	2.79	3.20	....	....	....	....
N	4.33	....	4.57	4.39	4.53	....
Br	49.53	....	....	....	....	49.25

3,5-Dibromphenylalanine is sparingly soluble in cold water but it dissolves in about 125 parts of water at 100°. It separates in long, hairy needles forming an extraordinary bulky mass, so that the beaker can be almost inverted. It is very sparingly soluble in boiling alcohol. Its aqueous solution tastes sweet and astringent. It melts with decomposition, to a red oil, at about 233°–234° when slowly heated. The point of decomposition depends considerably on the rate and manner of heating. It can be dried at 85°–90° but at 120° it gradually suffers decomposition.

Behavior of 3,5-Dibromphenylalanine toward Hydrochloric Acid and Barium Hydroxide.—3,5-Dibromphenylalanine can be heated for 6 hours in a sealed tube with hydrochloric acid (sp. gr. 1.19) at 130° apparently without suffering any significant decomposition.

Toward boiling concentrated solutions of barium hydroxide it is much less stable. When 0.3 gram of the acid was boiled with a barium hydroxide solution, saturated at 100°, for 8 hours, about eleven per cent of the bromine was found to have been removed, or in other words could be precipitated in nitric acid solution by adding silver nitrate.

The Dibromphenylalanine Hydrochloride, $Br_2C_6H_3CH_2CH(NH_2HCl)COOH$.—3,5-Dibromphenylalanine dissolves slowly on boiling with 10 per cent hydrochloric acid, and on cooling separates in clusters of long prisms. On adding strong hydrochloric acid and continuing the boiling, the crystals, without apparently going into solution, are transformed into stout prisms which seem to have a different habit. When these were dried over sulphuric acid they had the composition of a 1:1 salt. They melted at about 254° with effervescence. Like the hydrochloride of diiodtyrosine the salt is dissociated by water.

0.2216 gram substance required 6.5 cc. N/10 HCl.

0.1553 gram substance gave 0.0618 gram AgCl.

	Calculated for $C_9H_9O_2NBr_2.HCl$.	Found.
N	3.89	4.11
Cl	9.87	9.84

Barium Salt, $[Br_2C_6H_3CH_2CH(NH_2)COO]_2Ba.3H_2O$.—This characteristic salt readily separates when barium chloride is added to a solution of the acid in ammonia. It is sparingly soluble in cold water but dissolves quite readily in water at 100° and separates slowly in clusters of thin, colorless plates or blades with curved outline.

The water determinations on the air dried substance agreed for a salt containing 3 molecules of water of crystallization.

0.1157 gram substance lost 0.0074 gram H_2O at 100°.

0.0567 gram substance lost 0.0035 gram H_2O at 100°.

	Calculated for	Found.	
	$C_{18}H_{16}O_4N_2Br_4Ba.3H_2O$	I.	II.
H_2O	6.46	6.40	6.17

0.1081 gram substance dried at 100° gave 0.0320 gram $BaSO_4$.

	Calculated for $C_{18}H_{16}O_4N_2Br_4Ba$.	Found.
Ba	17.58	17.42

Carbon dioxide produces no precipitate in an aqueous solution of this salt.

The *silver salt* was prepared by dissolving 3,5-dibromphenylalanine in the calculated quantity of one-tenth normal potassium hydroxide and then adding silver nitrate in excess. The silver salt separated in the form of microscopic crystals which remained perfectly white when dried at 80°. It was insoluble in boiling water. It dissolved in an excess of ammonia with ease and it was readily soluble in dilute nitric acid, especially on warming. It could be boiled for several minutes with nitric acid of sp. gr. 1.42 without separating silver bromide.

Copper Salt, $[Br_2C_6H_3CH_2CH(NH_2)COO]_2Cu.1^1/_2H_2O$. — This salt was prepared by adding copper sulphate to an aqueous solution of the acid. It formed light blue scales or irregular plates and it was almost insoluble in boiling water. Air dried, it contained one and one-half molecules of water of crystallization.

0.3056 gram substance lost 0.0113 gram H_2O at 90°.

	Calculated for $C_{18}H_{16}O_4N_2Br_4Cu.1^1/_2H_2O$.	Found.
H_2O	3.67	3.70

0.0953 gram substance dried at 90° gave 0.0109 gram Cu_2S.

	Calculated for $C_{18}H_{16}O_4N_2Br_4Cu$.	Found.
Cu	8.97	9.15

3,5-Dibromphenylalanine Ethyl Ester, $Br_2C_6H_3CH_2CH(NH_2)COOC_2H_5$.—Five grams of finely pulverized dibromphenylalanine were suspended in absolute alcohol and dry hydrochloric acid gas passed through the solution to saturation without cooling. The substance rapidly went into solution. The solution was then evaporated to dryness under reduced pressure at a moderate temperature and the operation repeated. The alcohol was distilled off under reduced pressure, the crystalline residue taken up with cold water, and the free ester liberated with 33 per cent sodium hydroxide and shaken out with ether, while the solution was kept cold in a freezing mixture.

The ether extracts were shaken for 15 minutes with anhydrous potassium carbonate and then dried over sodium sulphate for 24 hours. The ether was distilled off and the ester distilled under diminished pressure. It boiled with very little decomposition and almost entirely between 234° and 237° at 24 mm. pressure. The weight of distilled ester collected was 4.2 grams, or 73 per cent of the calculated. This ester is a very thick oil with a faint, peculiar, aminelike odor. It is very difficultly soluble in water. For analysis is was converted into the picrate and the hydröchloride.

3,5-Dibromphenylalanine Ethyl Ester Picrate.—This substance separates when an aqueous solution of picric acid is added to an alcohol solution of the ester. It is very sparingly soluble in cold water but it dissolves in water at 100° and separates in large prisms which are irregular and very much etched. It melts at 181°–182° to a clear red oil, without significant effervescence.

I. 0.1163 gram substance required 8.1 cc. N/10 HCl.
II. 0.1388 gram substance required 9.6 cc. N/10 HCl.

	Calculated for $C_{11}H_{13}O_2NBr_2.C_6H_3O_7N_3$.	Found. I.	Found. II.
N	9.66	9.75	9.68

3,5-Dibromphenylalanine Ethyl Ester Hydrochloride.—This was prepared by adding alcohol saturated with hydrogen chloride to the ester. It was very soluble in alcohol but it crystallized from a mixture of alcohol and ether in needlelike prisms. It melted to a clear oil at 186°–187°.

0.1320 gram substance gave 0.0492 gram AgCl.
0.1800 gram substance required 4.7 cc. N/10 HCl.

	Calculated for $C_{11}H_{13}O_2NBr_2.HCl$.	Found.
Cl	9.16	9.21
N	3.61	3.65

Di(3,5-dibrombenzyl)malonic Ethyl Ester, $(Br_2C_6H_3CH_2)_2C(CO_2C_2H_5)_2$.—This compound is the chief product formed when 3,5-dibrombenzyl bromide and the sodium salt of ethyl malonate are allowed to act in molecular proportions in alcoholic solution. After heating for one hour on the steam bath the solution no longer reacted alkaline to turmeric. The sodium bromide was then filtered off, the alcohol removed by distillation, and the residue was stirred with cold water. The yield of the undissolved substance was 60 per cent of the calculated. After one crystallization from alcohol it melted constantly at 99°. The ester is insoluble in water and dilute alkali and it crystallizes from alcohol in needlelike prisms.

I. 0.2639 gram substance gave 0.3077 gram AgBr.
II. 0.2323 gram substance gave 0.2679 gram AgBr.

	Calculated for $C_{21}H_{20}O_4Br_4$.	Found. I.	II.
Br	48.78	49.64	49.07

3,5-Dibrombenzylphthalimide, $Br_2C_6H_3CH_2N(CO)_2C_6H_4$.—This was obtained by heating equal molecular proportions of potassium phthalimide and 3,5-dibrombenzyl bromide for a short time at 140°. It crystallizes from alcohol in colorless prisms melting at 185°.

I. 0.0846 gram substance gave 0.0805 gram AgBr.
II. 0.2882 gram substance gave 0.2729 gram AgBr.
III. 0.2598 gram substance gave 8.5 cc. of moist nitrogen at 18°.5 and 762 mm. pressure.

	Calculated for $C_{15}H_9O_2NBr_2$.	Found. I.	II.	III.
N	3.54	3.77	....	....
Br	40.51	....	40.50	40.28

New Haven, Conn.,
May, 1908.

CLX.—RESEARCHES ON PYRIMIDINES: SYNTHESIS OF 4-METHYLCYTOSINE.

[THIRTY-SEVENTH PAPER].

By Carl O. Johns.

There are two methyl derivatives of cytosine having the methyl group attached to carbon. Of these, 5-methylcytosine (Formula I.) has been described in the fifth paper of this series,[1] while a description of the synthesis and properties of 4-methylcytosine (V.) will be given in the following pages.

Acetoacetic ester condenses readily in an aqueous solution of sodium hydroxide with pseudoethylthiourea hydrobromide to give an excellent yield of 2-ethylmercapto-4-methyl-6-oxypyrimidine (II.). This compound has been prepared by List[2] but his method requires several days, and, calculating from the weight of acetoacetic ester used, the yields are only about one-half as great as those obtained by the method here described.

When 2-ethylmercapto-4-methyl-6-oxypyrimidine is boiled with phosphorus oxychloride it yields 2-ethylmercapto-4-methyl-6-chlorpyrimidine (III.). When heated in a sealed tube at 140°–150° with alcoholic ammonia the chlorine in this compound is replaced by an amino group and 2-ethylmercapto-4-methyl-6-aminopyrimidine (IV.) is obtained. This is readily converted into 4-methylcytosine (V.) by digesting with concentrated hydrochloric acid and precipitating the base with a slight excess of ammonium hydroxide.

The chloride (III.) reacts more readily with alcoholic sodium ethylate than it does with alcoholic ammonia. Action takes place at room temperature. Sodium chloride separates and 2-ethylmercapto-4-methyl-6-ethoxypyrimidine (VI.) is formed.

4-Methylcytosine can easily be distinguished from 5-methylcytosine. It does not melt at 310°, while 5-methylcytosine melts with effervescence at 270°. It is far less soluble in water than is 5-methylcytosine. Moreover, 4-methylcytosine crystallizes from water in long, anhydrous prisms, while 5-methylcytosine gives flat prisms containing one-half molecule of water.

4-Methylcytosine gives a very characteristic basic hydrochloride containing 3 molecules of base to 1 molecule of hydrogen chloride while 5-methylcytosine under similar conditions gives a hydrochloride containing 2 molecules of base to one of acid.

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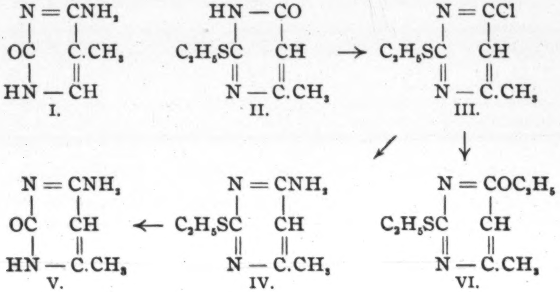
[1] Wheeler and Johnson: This Journal, **31**, 591 (1904).

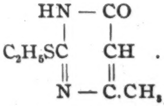
[2] Ann. Chem. (Liebig), **236**, 14 (1886).

When crystallized from concentrated solutions of the common acids, 4-methylcytosine gives a series of normal salts.

4-Methylcytosine has been used for the preparation of some purine derivatives to be described in another paper.



EXPERIMENTAL PART.

2-Ethylmercapto-4-methyl-6-oxypyrimidine,

—List[1] prepared this compound by heating 2-thio-4-methyl-6-oxypyrimidine with ethyl iodide in the presence of sodium ethylate. It can be obtained more easily and in better yields by condensing pseudoethylthiourea hydrobromide with acetoacetic ester in an aqueous solution of sodium hydroxide. This condensation is very smooth and the yields range from 80 to 90 per cent of the theoretical quantity.

Ninety-three grams of pseudoethylthiourea hydrobromide are dissolved in 100 cc. of water and this solution is mixed with 65 grams of acetoacetic ester. To this mixture is slowly added a solution of 40 grams of sodium hydroxide in 80 cc. of water. Condensation takes place at once, but to insure complete reaction the mixture is allowed to stand at room temperature overnight. When the resulting clear solution is acidified with acetic acid about 75 grams of 2-ethylmercapto-4-methyl-6-oxypyrimidine are obtained. When crystallized from dilute alcohol it melts at 144°–145° and possesses all the properties of List's compound.

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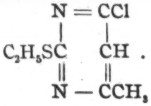
[1] Ann. Chem. (Liebig), **236**, 14 (1886).

Analyses (Kjeldahl):

	Calculated for $C_7H_{10}ON_2S$.	Found. I.	II.
N	16.47	16.49	16.52

2-Ethylmercapto-4-methyl-6-chlorpyrimidine,

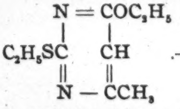


—Twenty grams of 2-ethylmercapto-4-methyl-6-oxypyrimidine were heated with 60 cc. of phosphorus oxychloride in an oil bath kept at 130°–135° until hydrogen chloride was no longer evolved. The excess of phosphorus oxychloride was removed under diminished pressure and the resulting thick oil was poured on cracked ice. The chloride was extracted with ether and dried over calcium chloride. When the ether was evaporated a clear, red oil remained. This boiled at 142° at 15 mm. pressure. The yield of pure chloride was about 75 per cent of the calculated quantity. This chloride is very stable towards water and alcohol.

Analyses (Kjeldahl):

	Calculated for $C_7H_9N_2SCl$.	Found. I.	II.
N	14.85	14.71	15.09

2-Ethylmercapto-4-methyl-6-ethoxypyrimidine,



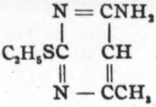
.—An ether solution of 2-ethylmercapto-4-methyl-6-chlorpyrimidine was added to alcohol containing an excess of sodium, calculating from the chloride. An immediate reaction took place with the liberation of heat.

The excess of alcohol was evaporated, and, after adding water, the oil was shaken out with ether and dried over calcium chloride. When the ether was evaporated an oil remained. This boiled at 154° at 20 mm. pressure.

Analyses (Kjeldahl):

	Calculated for $C_9H_{14}ON_2S$.	Found. I.	II.
N	14.14	14.08	14.43

2-Ethylmercapto-4-methyl-6-aminopyrimidine,

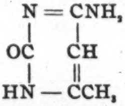


.—Alcoholic ammonia does not react at room temperature with 2-ethylmercapto-4-methyl-6-chlorpyrimidine. Sixteen grams of the chloride were heated in a sealed tube for 4 hours at 140°–150° with about 75 cc. of alcoholic ammonia saturated at 0°. The tube, wheen cooled, was lined with ammonium chloride and crystals of the new amino compound. The reaction was very smooth and the alcohol remained colorless. After evaporating to dryness, the residue was washed with cold water and recrystallized from dilute alcohol. The crystals melted at 115°–116° to a clear oil. They have a tetrahedral outline and show a great tendency to twin. They are easily soluble in cold alcohol and acetic acid, moderately soluble in cold benzene, and difficultly soluble in boiling water.

Analyses (Kjeldahl):

	Calculated for $C_7H_{11}N_3S$.	Found. I.	II.
N	24.85	24.83	25.07

4-Methylcytosine,



. — When 2-ethylmercapto-4-methyl-6-aminopyrimidine is evaporated with concentrated hydrochloric acid ethyl mercaptan is evolved and an almost theoretical yield of 4-methylcytosine monohydrochloride is obtained. The base is obtained from this salt by adding an excess of ammonium hydroxide. 4-Methylcytosine crystallizes from water in anhydrous, slender, brittle prisms. These crystals do not melt at 310°, but decompose slowly without effervescence at higher temperatures. 4-Methylcytosine is moderately soluble in boiling water. At 24°, 0.36 gram is dissolved by 100 cc. of water. It is soluble in cold aqueous ammonia and in cold acetic acid.

Analyses (Kjeldahl):

	Calculated for $C_5H_7ON_3$.	Found.	
		I.	II.
N	33.60	33.52	33.39

4-Methylcytosine Monohydrochloride, $C_5H_7ON_3.HCl$.—This salt is obtained when 2-ethylmercapto-4-methyl-6-aminopyrimidine is digested with concentrated hydrochloric acid. It is also formed by crystallizing 4-methylcytosine from 20 per cent hydrochloric acid. It is moderately soluble in hot hydrochloric acid and separates on cooling in blunt, flat prisms with a hexagonal appearance. When dried over potassium hydroxide it does not lose water at 110°. In a capillary tube it begins to shrivel at about 280° and decomposes slowly above 300°.

Analyses:

	Calculated for $C_5H_7ON_3.HCl$.	Found.	
		I.	II.
N	26.00	26.10	26.09
Cl	21.98	21.81	....

The anhydrous monohydrochloride of 4-methylcytosine is also obtained unaltered when its aqueous solution is saturated with hydrogen chloride and evaporated in a desiccator. The crystals thus obtained did not lose weight at 125°.

Analysis:

	Calculated for $C_5H_7ON_3.HCl$.	Found.
Cl	21.98	21.95

4-Methylcytosine Basic Hydrochloride, $(C_5H_7ON_3)_3.HCl$.—Such a salt was formed when a hot aqueous solution of 0.25

gram of the base was mixed with an aqueous solution of 0.32 gram of the monohydrochloride. The basic salt separated in scales with a pearly lustre. These began to shrivel at about 270° and turned brown above 280° but did not melt at 310°. These crystals lost weight when dried at 130°–140°, but attempts to determine water of crystallization gave results that differed widely, but indicated that one molecule of water was probably present. The dried salt contained 3 molecules of the base and 1 molecule of hydrogen chloride. This same salt was obtained when equal weights of the base and monohydrochloride were recrystallized from water.

Analyses of the dried salt:

	Calculated for $(C_5H_7ON_3)_3.HCl$.	Found.		
		I.	II.	III.
N	30.61	....	30.26	....
Cl	8.62	8.51	.....	8.49

4-Methylcytosine Nitrate, $C_5H_7ON_3.HNO_3$.—One-half gram of 4-methylcytosine was crystallized from 10 cc. of 25 per cent nitric acid. The salt separated in round clusters of blunt prisms. It did not contain water of crystallization.

0.0983 gram of substance gave 25.2 cc. of moist nitrogen at 18° and 770 mm. pressure.

	Calculated for $C_5H_7ON_3.HNO_3$.	Found.
N	29.79	29.94

4-Methylcytosine Sulphate, $(C_5H_7ON_3)_2.H_2SO_4.H_2O$.—When 4-methylcytosine was crystallized from 25 per cent sulphuric acid, two molecules of the base united with one molecule of sulphuric acid to form a normal sulphate containing one molecule of water of crystallization. The crystals were large, flat prisms that did not lose water at 110°, but lost one molecule of water slowly at 160°–170°.

Analyses:

	Calculated for $(C_5H_7ON_3)_2.H_2SO_4.H_2O$.	Found.		
		I.	II.	III.
H_2O	4.91	....	4.83	....
N	22.95	22.79	....	22.82
S	8.74	....	8.88	....

4-Methylcytosine Picrate, $C_5H_7ON_3.C_6H_2(NO_2)_3OH$.—When an aqueous solution of picric acid is added to a solution of 4-methylcytosine, an immediate precipitate is obtained. This picrate is difficultly soluble in hot water and crystallizes in beautiful, yellow needles that turn brown at about 265° and decompose slowly above that temperature.

0.0858 gram of substance gave 17.3 cc. of moist nitrogen at 18° and 772 mm. pressure.

	Calculated for $C_5H_7ON_3.C_6H_2(NO_2)_3OH$.	Found.
N	23.73	23.65

New Haven, Conn.,
May, 1908.

THE CONDUCTIVITY AND IONIZATION OF ELECTROLYTES IN AQUEOUS SOLUTIONS AS CONDITIONED BY TEMPERATURE, DILUTION, AND HYDROLYSIS.

By Harry C. Jones and C. A. Jacobson.

Introduction.

It is now generally recognized that chemical activity is conditioned primarily by the number of reacting parts or ions. Therefore, any method by which the number of ions can be determined or, in other words, any method that gives the percentage dissociation of a compound, is of fundamental importance. Of the three or four methods now in use for determining ionization, the electrical conductivity method is doubtless the most general, and possibly the most reliable.

That the conductivity of electrolytes is influenced by temperature has been known for about fifty years.

Beetz,[1] in 1862, was the first to arrive at any definite relation between temperature and conductivity, although Hankel,[2] Marie-Davy,[3] Becquerel,[4] and a few others had previously made some observations which led them to conclude that the conductivity of electrolytes increases with rise in temperature. Beetz worked with zinc sulphate from 1° to 24°, at various concentrations, and arrived at the formula

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[1] Pogg. Ann., **117**, 1 (1862).

[2] *Ibid.*, **69**, 255 (1846).

[3] Compt. rend., **54**, 465.

[4] Pogg. Ann., **70**, 254 (1847).

$$Z = 32.09 + 4.0346p - 0.04073p^2$$

as expressing the relation between temperature and conductivity. (p is the percentage concentration of anhydrous zinc sulphate.) He thus concluded that the conductivity increases proportionally with rise in temperature, except at high dilutions. Beetz also observed a maximum in the conductivity curve, with changing concentration, and noticed that this maximum varied with change in temperature. In 1879 Freund[1] repeated the experiments of Beetz and found the same relations to hold, but his results were about 5 per cent higher. Other investigators in this field are: Berggren,[2] Lentz,[3] and Sack.[4] The last-named found a sharp maximum conductivity in three different concentrations of copper sulphate.

Grotrian,[5] in 1874, investigated the effect of temperature on the conductivity of sulphuric and hydrochloric acids, from 8° to 70°, at different dilutions, and concluded that conductivity is a linear function of the temperature. The following year Kohlrausch and Grotrian[6] made a comprehensive study of this field, using numerous salts and acids at temperatures ranging between 0° and 40°, and deduced the following formula as expressing the relation between temperature and conductivity:

$$K_t = K_0(1 + \alpha t + \beta t^2),$$

in which K represents the conductivity, t the temperature, and α and β constants of different orders of magnitude, as found by experiment. They calculated the temperature coefficients at 18° by the equation

$$\left(\frac{1}{K}\frac{dK}{dt}\right)_{18} = \frac{\alpha + 2\beta.18}{1 + \alpha.18 + \beta.18^2},$$

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[1] Wied. Ann., **7,** 49 (1879).

[2] *Ibid.*, **1,** 499 (1877).

[3] Bull. Acad. Imp. Sci., St. Petersb., **10,** 299.

[4] Wied. Ann., **43,** 212 (1891).

[5] Pogg. Ann., **151,** 378 (1874).

[6] *Ibid.*, **154,** 215 (1875).

in which the symbols have the same meaning as above. From this work they concluded that the conductivity of dilute solutions is not a linear function of the temperature, as was originally thought, but a *parabolic one.* They also observed a maximum conductivity for hydrochloric acid when the concentration was about 30 per cent. In 1885 Kohlrausch[1] represented conductivity graphically as the cube root of the concentration. In other words, he made μ_v the ordinate and $\sqrt[3]{1/v}$ the abscissa.

Up to this time no exception had been found to the general principle that the conductivity of electrolytes in aqueous solution increases with rise in temperature, and also with increase in dilution where the concentration is less than 0.1 normal. Arrhenius,[2] in 1889, was the first to notice an exception. He found that the conductivity of phosphoric and hypophosphorous acids decreases with rise in temperature, between 25° and 95°. Sack[3] and others have since observed negative temperature coefficients, but more especially with organic solvents. The explanation hitherto offered for the rapid increase in conductivity with rise in temperature is that dissociation increases as the temperature increases. In other words, the higher the temperature the larger the number of ions present for a given concentration and, consequently, a resulting increase in conductivity. The fact that Arrhenius found a diminishing dissociation with rise in temperature led others to work along this line.

In 1890 Krannhals[4] took up the problem and measured the conductivity of a number of acids and salts at the following temperatures: 18°, 50°.3, 82°, and 99°.4. He found that the conductivity increases as a linear function of the dilution, and a parabolic function of the temperature, except for magnesium sulphate and potassium ferrocyanide, where the increase is abnormally great. The reason for this increase in conductivity with rise in temperature he ascribed to diminishing viscosity of the solvent. In some cases he

[1] Wied. Ann., **26**, 197 (1885).

[2] Z. physik. Chem., **4**, 96 (1889).

[3] *Loc. cit.*

[4] Z. physik. Chem., **5**, 250 (1890).

observed a decrease in dissociation with rise in temperature, but concluded that this must be due to experimental error.

The same year J. Trötsch[1] undertook an investigation to ascertain the influence of water of crystallization on the conductivity of electrolytes, and arrived at the conclusion that the conductivity of those substances which do not crystallize with water increases regularly or remains constant with rise in temperature, while in the case of those substances that crystallize with water, the rate of increase of conductivity grows less as the temperature rises, as well as with increase in dilution. He also noticed that the temperature coefficients of cupric chloride, at all concentrations, increase from 0° to 40°, and then decrease. He noticed a sudden change in color from green to blue in an 18.2 per cent solution of cupric chloride, and from red to blue at different concentrations of cobalt chloride above 100°. He explained these phenomena as being due to a loss of the water of hydration. He also concluded, as many before him had done, that increase in temperature increases the dissociation.

In 1891 Douglas[2] worked with several acids, bases, and salts at temperatures ranging from 0° to 35°. From his work he drew the conclusion that dissociation is independent of temperature. The same conclusion was reached by Wood[3] and Jahn,[4] although the results of the former indicate just the opposite. Jahn, however, admitted that his results, in the case of valeric acid, showed a diminishing dissociation with rise in temperature, but thought that this was probably due to experimental error.

In 1900 Whetham[5] determined the ionization of a few strongly dissociated acids and salts at 0° by the freezing point method. After comparing his results with those of Kohlrausch, he concluded that the dissociation is greater at 0° than at 18°.

[1] Wied. Ann., **41**, 259 (1890).

[2] THIS JOURNAL, **26**, 428 (1891).

[3] Phil. Mag., **41**, 117 (1896).

[4] Z. physik. Chem., **16**, 72 (1895).

[5] *Ibid.*, **33**, 344 (1900).

The more recent investigations of Euler,[1] Schaller,[2] Noyes,[3] and West,[4] however, all point to the conclusion that dissociation diminishes with rise in temperature. Euler worked with a number of organic acids at eight temperatures ranging between 0° and 50°. Schaller studied organic acids and salts at temperatures ranging between 25° and 99°. In addition to observing that dissociation decreases with rise in temperature, he noticed that when the electrolytes are completely dissociated, the increase in conductivity is very nearly a linear function of the temperature. This was contrary to the observation of Kohlrausch and Grotrian referred to above.

An enormous amount of conductivity work has been done besides that already mentioned, but no reference will be made to work carried out at only one temperature, or where solvents other than water have been used, since that would not properly come within the scope of this paper.

We may summarize the results hitherto obtained as follows:

(1) The conductivity increases with rise in temperature.

(2) Conductivity increases with increase in dilution.

(3) Dissociation increases with increase in dilution.

Considering the number of conflicting results on the following points, we are inclined to believe that further confirmatory evidence is necessary before some of them are fully established:

(1) Dissociation decreases with rise in temperature.

(2) Conductivity is a linear function of the temperature.

(3) Conductivity is a cube root function of the concentration.

Some time after the publication of West's work, Jones[5] pointed out certain relations existing between the temperature coefficients of electrolytes and their hydrating power. Using West's results he showed that those electrolytes with no hydrating power have smaller temperature coefficients than those with large hydrating power, and that the order of the temperature coefficients will, in a measure, determine the hydrating power of the electrolyte. The close relation existing between the water of hydration and water of crystallization of a compound is seen from the work of Jones and his students.[1]

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[1] Z. physik. Chem., **21,** 257 (1896).

[2] *Ibid.*, **25,** 497 (1898).

[3] J. Am. Chem. Soc., **26,** 134 (1904).

[4] This Journal, **34,** 357 (1905).

[5] *Ibid.*, **35,** 445 (1905).

Purpose of this Investigation.

From the brief historical sketch here given, it is seen that the conclusions drawn regarding the influence of temperature upon dissociation are very conflicting, and that they need further experimental verification before they can be considered as fully established. The present work was undertaken to supply some such evidence; and, further, to extend the investigation to a larger number of inorganic compounds than was done by West, as well as to include some typical organic acids, to test the relations pointed out by Jones[2] between the temperature coefficients of conductivity of electrolytes and their hydrating power.

Method Employed.

The present work is, broadly speaking, a continuation of that by Jones and West,[3] and the method is essentially the same as the one that they employed.

Apparatus.—Eight conductivity cells of the form used in this laboratory were employed. The conductivities were read at eight concentrations, ranging from N/2 to N/2048, according to the Ostwald scheme of dilution. One cell was employed for each dilution.

The well-known Kohlrausch method, consisting of a Wheatstone bridge, resistance box, telephone, and an induction coil supplying the alternating current, was employed for reading the conductivities. The calibration of the bridge wire, resistance box, and thermometers was done in essentially the same way as that described by Jones and West. Moreover, it was considered advisable to keep the same range of temperature as they did, namely 0°, 10°, 25°, and 35°.

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[1] Carnegie Monograph No. 60 (Hydrates in Solution), 1906.

[2] This Journal, **35**, 445 (1905).

[3] *Ibid.*, **34**, 357 (1905).

In order to bring the cells containing the solutions to these temperatures, constant-temperature water baths were employed. We found that the zero bath described by West

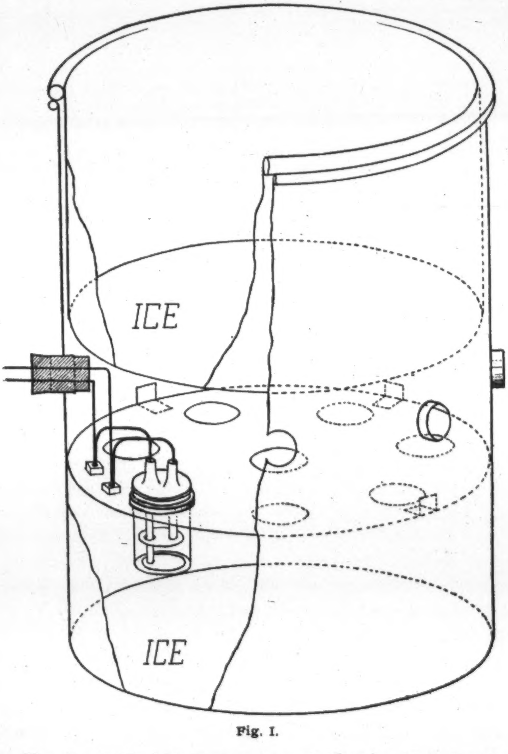

Fig. I.

gave conductivities that were invariably too high by about 0.5 per cent, and the difficulty was thought to lie in the fact that the upper portion of the cell was exposed to a much higher temperature, and, consequently, heat would be conducted into the solution, especially by the mercury of the electrodes. To overcome this difficulty, we constructed another form of ice bath, shown in the accompanying cut, Fig. I. By this means the air above and in immediate contact with the cells could also be brought to zero temperature. The whole apparatus was surrounded by hair packing, and well protected against conduction of heat from surrounding objects. This form of ice bath gave entirely satisfactory results.

The temperature of the 10° bath was regulated by a small gas burner and running hydrant water, stirred by a hot-air engine. We found that the temperature of the hydrant water did not remain constant long enough to answer our purpose without this regulation. Instead of using the Ostwald thermoregulator for the 25° and 35° baths, as was done by West, we obtained better results by simply regulating the flame of a small gas burner by hand. The water in these two baths was also stirred as above indicated.

The burettes and measuring flasks were calibrated for 20° by weighings reduced to the vacuum standard.

Water.—The conductivity water employed in this laboratory[1] was used in preparing the solutions. In order to obtain the true value for the conductivity of the electrolyte, a correction term must, of course, be applied for the conductivity of the solvent. Where the dilution is high this correction has a considerable value. The temperature coefficients of conductivity of water are also large, and this fact must be taken into account wherever conductivities are read at more than one temperature.

Although the marked influence of temperature on the conductivity of water had been pointed out by Pfeiffer[2], Kohlrausch,[3] and Schaller,[4] yet very few of the experimenters working in this field state that this fact was taken into account.

[1] THIS JOURNAL, **19**, 91 (1897).
[2] Wied. Ann., **31**, 831.
[3] Z. physik. Chem., **14**, 324 (1894).
[4] *Ibid.*, **25**, 497 (1898).

Euler[1] gives his reason for not applying the correction for water. Kohlrausch and Heydweiller found that the increase in the conductivity of water with rise in temperature was more rapid at higher than at lower temperatures. Schaller's results indicate a linear relation between conductivity and temperature from 25° to 99°. The latter relation has been found to hold in our work with numerous samples of water. A few of the results obtained with water investigated during the progress of this work are plotted in the accompanying diagram, where temperatures are the abscissae, and conductivities $\times 10^{-6}$ the ordinates.

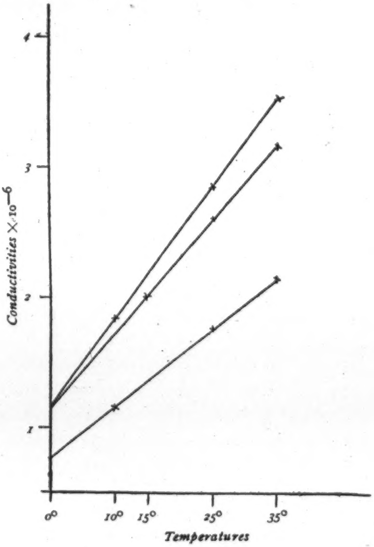

Fig. II.

Solutions.—The purest obtainable materials were used in the preparation of the solutions. However, before the salts were used they were carefully tested for impurities, and in most cases recrystallized one or more times. Except in a few cases, where the compounds are stable in the air, the solutions were all standardized by analysis. The organic acids, the purity of which had first been tested by determining their melting points, were standardized volumetrically with an aqueous solution of potassium hydroxide, which had been especially prepared and purified. The solutions were then made up by diluting the more concentrated with water, and bringing them to the calibration temperature.

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[1] *Loc. cit.*

Cell Constants.—For determining the cell constants, we took ($129.7 + \mu$ for water) as the conductivity of a N/50 solution of potassium chloride at 25° as the basis of our calculations. The purest obtainable potassium chloride was tested and further purified by fractional crystallization before it was used in the preparation of the above-mentioned standard solution. With this solution the cell constants of the first four cells were determined. Then a N/500 solution was prepared from the N/50 and its conductivity found by using the four cells whose constants had been determined. The value thus obtained for μ of the more dilute solution was used in determining the cell constants of the remaining four cells. The cell constants were redetermined every three or four weeks throughout the year. Ordinarily, no change in the cell constants amounting to more than 0.2 to 0.3 per cent was found.

For the purpose of checking the cell constants at 0°, we determined the following values of μ for potassium chloride: N/500 at 25° = 137.7, N/50 at 0° = 71.45, N/500 at 0° = 75.63. These are the averages of a large number of determinations, none of which varied more than 0.5 per cent from the others. To obtain the true values for any one of these solutions, the proper value for μ of water must be added.

Units.—To be consistent with the work previously done in this laboratory the results are expressed in Siemens units, and all conductivities here referred to are molecular conductivities—gram-molecular weights having been used in making up the solutions.

Results.—The results are expressed in the following tables. The molecular conductivities (μ_v) at the four temperatures indicated were calculated from the equation

$$\mu_v = K \frac{Va}{Rb}$$

where K is the cell constant, V the volume concentration, R the resistance, a and b the two arms of the bridge. The percentage dissociation (α) was calculated from the equation

$$\alpha = \frac{100.\mu_v}{\mu_\infty},$$

where μ_∞ is the conductivity at complete dissociation, or the highest value for μ_v obtained for the strongly dissociated electrolytes in which no hydrolysis is known to have taken place. When hydrolysis did take place, as, for example, with ferric chloride, as well as in the case of the weakly dissociated organic acids, α was calculated from Kohlrausch's law, $\mu_\infty = c + a$, where c and a represent the velocities of the cation and anion, respectively. The temperature coefficients, expressed in conductivity units between the temperatures indicated, were calculated from the formula

$$\frac{(\mu_v)_{t_1} - (\mu_v)_t}{t_1 - t},$$

in which $(\mu_v)_{t_1}$ represents μ_v at the higher temperature (t_1) and $(\mu_v)_t$ at the lower temperature (t), while the same coefficients expressed in percentages were calculated from the formula

$$\frac{(\mu_v)_{t_1} - (\mu_v)_t}{t_1 - t} \times \frac{100}{(\mu_v)_t}.$$

For each conductivity measurement given in the tables, three readings were taken, changing the resistance in the resistance box so as to bring the node on the bridge as near to the 40, 50, and 60 cm. marks as practicable. The mean of these was taken as the final reading. Whenever any irregularities appeared, either in the conductivities or in the temperature coefficients, the same readings were repeated one or more times on following days.

Sources of Error.

It may be well to call attention to some of the more important sources of error that must be taken into account in all conductivity work. In the first place, a sharp minimum in the telephone is not secured unless the electrodes are clean and well covered by a layer of platinum black or "platinum white." A small amount of an oily constituent is present in ordinary distilled water, and where the electrodes are left overnight in such water a small residue will be left on them, as is often seen deposited on the inside walls of wash-bottles, etc. It may take weeks before this becomes perceptible, but it should be taken into account.

At temperatures above 25° air bubbles are often found to gather on the electrodes, as has been pointed out by Jones and West. These not only interfere with the minimum in the telephone but may also affect the conductivity. After trying various methods for obviating this difficulty we found that the most satisfactory one was to heat the bath a few degrees above the temperature at which the conductivities are to be read, and after the bubbles have collected for a time, to raise the electrodes out of the solution, then returning them at once and cooling down the bath to the required temperature. When this is done the cells may be kept for any desired length of time at the temperature in question without any sign of a bubble appearing.

Another source of error often arises in assuming that the cells have attained the temperature of the bath before they have actually done so.

When small resistances are to be measured it is of the utmost importance to have the plugs in the resistance box absolutely clean, since a very small quantity of foreign matter on a plug will accumulate on the small resistance read, and will often amount to several per cent.

When working at temperatures above that of the room, a source of error that must not be overlooked is the condensation of the solvent on the glass stopper of the cell, thus concentrating the solution.

A formidable source of error is found in hydrolysis taking place to a greater or less extent in dilute solutions. This, of course, increases the conductivity to an enormous extent, as is seen especially in the case of iron salts. For this reason it becomes impossible to find μ_∞ for such compounds by the conductivity method directly, and the true value of μ_∞ for other electrolytes is called into question, since we are unable to tell to what extent hydrolysis has taken place.

Lithium Chloride.

Table I.—Molecular Conductivity and Dissociation.

	0°.		11°.2.		25°.		35°.	
V.	μ_v.	α.	μ_v.	α.	μ_v.	α.	μ_v.	α.
2	41.33	72.1	55.26	70.3	75.79	68.7	91.71	68.5
8	47.27	82.4	64.18	81.6	88.41	80.1	105.9	79.1
16	49.20	85.8	67.33	85.6	92.89	85.1	112.3	83.9
32	51.11	89.1	69.91	88.9	96.24	87.2	116.4	86.9
128	53.96	94.1	73.92	94.0	101.5	91.9	122.9	91.8
512	55.55	96.9	77.52	97.0	106.3	96.6	128.6	96.0
1024	56.08	97.8	77.62	98.7	107.2	97.1	130.3	97.3
2048	57.34	100.0	78.64	100.0	110.4	100.0	133.9	100.0

Table III.—Temperature Coefficients.

	0° to 11°.2.		11°.2 to 25°.		25° to 35°.	
V.	Cond. units.	Per cent.	Cond. units.	Per cent.	Cond. units.	Per cent.
2	1.24	3.00	1.49	2.69	1.59	2.10
8	1.51	3.41	1.75	2.72	1.75	1.98
16	1.62	3.39	1.85	2.75	1.94	2.09
32	1.68	3.29	1.91	2.73	2.02	2.10
128	1.79	3.32	2.00	2.70	2.14	2.11
512	1.90	3.42	2.08	2.69	2.23	2.10
1024	1.92	3.42	2.15	2.77	2.31	2.15
2048	....	....	2.28	2.90	2.35	2.13

Lithium Bromide.

Table IV.—Molecular Conductivity.

V.	0°.	9°.3.	25°.	35°.
2	44.83	55.94	78.52	96.02
8	49.84	63.42	89.78	109.5
16	51.51	66.75	95.03	114.9
32	53.10	68.77	98.66	119.5
128	56.57	73.70	106.7	128.6
512	57.44	75.06	108.2	130.6
1024	57.97	75.99	109.9	133.3
2048	61.05	80.68	114.8	138.3

Table V.—Percentage Dissociation.

V.	0°.	9°.3.	25°.	35°.
2	73.4	69.3	68.4	69.4
8	81.6	78.6	78.2	79.2
16	84.4	82.7	82.8	83.1
32	87.0	85.2	85.9	86.4
128	92.7	91.4	92.9	93.0
512	94.1	93.0	94.3	94.4
1024	95.0	94.2	95.7	96.4
2048	100.0	100.0	100.0	100.0

Table VI.—Temperature Coefficients.

	0° to 9°.3.		9°.3 to 25°.		25° to 35°.	
V.	Cond. units.	Per cent.	Cond. units.	Per cent.	Cond. units.	Per cent.
2	1.19	2.66	1.43	2.56	1.75	2.23
8	1.46	2.93	1.67	2.63	1.97	2.19
16	1.63	3.16	1.80	2.70	1.99	2.09
32	1.68	3.16	1.90	2.91	2.08	2.11
128	1.84	3.25	2.10	2.85	2.19	2.05
512	1.89	3.29	2.11	2.81	2.24	2.07
1024	1.94	3.35	2.16	2.84	2.34	2.13
2048	2.33	3.82	2.17	2.68	2.35	2.05

Lithium Nitrate.

Table VII.—Molecular Conductivity.

V.	0°.	10°.	25°.	35°.
2	38.65	52.28	70.56	82.20
8	43.83	57.79	79.71	96.99
16	45.96	60.32	84.16	100.9
32	47.27	62.51	87.39	105.1
128	51.05	66.88	93.29	112.2
512	51.53	68.07	96.03	115.6
1024	52.00	69.47	98.01	117.8
2048	52.40	70.01	100.03	121.0

Table VIII.—Percentage Dissociation.

V.	0°.	10°.	25°.	35°.
2	73.8	74.7	70.4	67.9
8	83.6	82.5	79.5	80.2
16	87.7	86.2	83.9	83.4
32	90.2	89.3	87.1	86.9
128	97.4	95.5	93.0	92.7
512	98.3	97.2	95.7	95.5
1024	99.2	99.2	97.7	97.4
2048	100.0	100.0	100.0	100.0

Table IX.—Temperature Coefficients.

	0° to 10°.		10° to 25°.		25°. to 35°	
V.	Cond. units.	Per cent.	Cond. units.	Per cent.	Cond. units.	Per cent.
2	1.26	3.26	1.35	2.58	1.64	2.32
8	1.40	3.19	1.46	2.53	1.67	2.09
16	1.44	3.13	1.59	2.64	1.70	2.02
32	1.52	3.22	1.66	2.67	1.77	2.03
128	1.58	3.10	1.76	2.63	1.89	2.03
512	1.65	3.20	1.86	2.73	1.96	2.04
1024	1.75	3.36	1.90	2.73	1.98	2.02
2048	1.76	3.36	2.02	2.89	2.07	2.06

Lithium Sulphate.

Table X.—Molecular Conductivity.

V.	0°.	9°.6.	25°.	35°.
2	47.08	61.97	89.59	107.5
8	66.74	88.18	128.4	154.9
16	75.50	100.2	144.5	175.3
32	82.15	109.5	159.3	194.0
128	96.81	129.0	188.5	230.3
512	104.6	139.1	202.8	248.3
1024	108.1	143.8	211.4	258.8
2048	111.8	148.0	219.5	268.0

Table XI.—Percentage Dissociation.

V.	0°.	9°.6.	25°.	35°.
2	42.1	41.9	40.8	40.1
8	59.7	59.6	58.5	57.8
16	67.5	67.7	65.8	65.4
32	73.5	74.0	72.6	72.4
128	86.6	87.2	85.9	85.9
512	93.6	94.0	92.4	92.7
1024	96.7	97.2	96.3	96.6
2048	100.0	100.0	100.0	100.0

Table XII.—Temperature Coefficients.

	0° to 9°.6.		9°.6 to 25°.		25° to 35°.	
V.	Cond. units.	Per cent.	Cond. units.	Per cent.	Cond. units.	Per cent.
2	1.55	3.29	1.68	2.71	1.79	2.00
8	2.23	3.34	2.25	2.55	2.65	2.06
16	2.57	3.40	2.88	2.87	3.08	2.13
32	2.85	3.47	3.23	2.96	3.47	2.18
128	3.35	3.46	3.86	2.99	4.18	2.22
512	3.59	3.43	4.14	2.98	4.55	2.25
1024	3.72	3.41	4.39	3.05	4.74	2.24
2048	3.77	3.37	4.64	3.13	4.85	2.21

Sodium Nitrate.

Table XIII.—Molecular Conductivity and Percentage Dissociation.

	0°.		25°.		35°.	
V.	μ_v.	α.	μ_v.	α.	μ_v.	α.
2	43.34	72.3	78.1	67.0	91.7	65.0
8	50.27	83.9	90.9	77.9	111.3	78.9
16	52.57	86.1	97.5	83.6	117.5	83.3
32	55.38	92.4	101.3	86.9	122.5	86.9
128	59.28	98.9	107.7	92.3	128.9	91.4
512	59.34	99.0	111.3	95.5	134.8	95.6
1024	59.39	99.8	114.0	97.8	138.5	98.2
2048	59.93	100.0	116.6	100.0	141.0	100.0

Table XIV.—Temperature Coefficients.

	0° to 25°.		25° to 35°.	
V.	Cond. units.	Per cent.	Cond. units.	Per cent.
2	1.39	3.21	1.36	1.74
8	1.62	3.22	2.04	2.24
16	1.79	3.41	2.00	2.44
32	1.83	3.30	2.12	2.05
128	1.94	3.27	2.12	1.94
512	2.08	3.51	2.35	2.11
1024	2.18	3.68	2.45	2.15
2048	2.27	3.79	2.44	2.09

Disodium Phosphate.

Table XV.—Molecular Conductivity and Percentage Dissociation.

	0°.		25°.		30°.	
V.	μ_v.	α.	μ_v.	α.	μ_v.	α.
16	67.3	68.8	133.4	72.5	148.6	72.1
32	75.0	81.5	147.8	80.3	164.5	79.8
128	88.4	96.1	168.6	91.5	188.1	91.2
512	91.7	99.7	182.3	99.1	203.8	98.8
1024	91.9	99.9	183.7	99.8	205.2	99.5
2048	92.0	100.0	184.0	100.0	206.2	100.0

Table XVI.—Temperature Coefficients.

	0° to 25°.		25° to 30°.	
V.	Cond. units.	Per cent.	Cond. units.	Per cent.
16	2.64	4.17	3.04	2.28
32	2.91	3.88	3.34	2.26
128	3.21	3.63	3.90	2.32
512	3.62	3.95	4.30	2.35
1024	3.67	3.99	4.30	2.34
2048	3.68	4.00	4.44	2.41

Potassium Sulphocyanate.

Table XVII.—Molecular Conductivity.

V.	0°.	13°.5.	25°.	30°.
2	57.75	79.47	100.0	110.2
8	62.48	87.87	110.9	121.9
16	64.26	90.81	115.4	126.8
32	65.99	93.39	118.7	130.8
128	70.70	100.1	127.3	139.4
512	71.28	101.2	129.8	142.3
1024	72.25	102.6	131.5	144.3
2048	72.86	103.0	133.7	147.3

Table XVIII.—Percentage Dissociation.

V.	0°.	13°.5.	25°.	30°.
2	79.3	77.2	74.8	74.8
8	85.8	85.3	83.0	82.8
16	88.2	88.2	86.3	86.1
32	90.6	90.7	88.8	88.8
128	97.0	97.2	95.2	94.6
512	97.8	98.3	97.1	96.6
1024	99.2	99.6	98.4	98.0
2048	100.0	100.0	100.0	100.0

Table XIX.—Temperature Coefficients.

	0° to 13°.5.		13°.5 to 25°.		25° to 30°.	
V.	Cond. units.	Per cent.	Cond. units.	Per cent.	Cond. units.	Per cent.
2	1.31	2.27	1.78	2.24	2.04	2.04
8	1.88	3.00	2.00	2.28	2.20	1.98
16	1.97	3.07	2.14	2.36	2.28	1.98
32	2.04	3.09	2.18	2.33	2.41	2.03
128	2.18	3.08	2.38	2.38	2.42	1.90
512	2.23	3.13	2.46	2.43	2.50	1.93
1024	2.26	3.13	2.49	2.43	2.56	1.95
2048	2.24	3.07	2.60	2.52	2.72	2.03

Potassium Chromate.

Table XX.—Molecular Conductivity.

V.	0°.	12°.2.	25°.	35°.
2	96.50	128.1	165.7	197.5
8	111.3	151.9	196.0	235.4
16	117.8	163.5	213.5	256.0
32	124.6	173.7	227.2	272.0
128	140.1	191.1	252.9	303.0
512	147.1	205.5	272.0	327.8
1024	150.1	209.2	276.2	330.2
2048	151.4	211.5	279.9	334.3

Table XXI.—Percentage Dissociation.

V.	0°.	12°.2.	25°.	35°.
2	63.7	60.6	59.2	59.6
8	73.5	71.8	70.0	70.4
16	77.8	77.3	76.3	76.6
32	82.3	82.1	81.2	81.4
128	92.5	90.4	90.4	90.6
512	97.2	97.2	97.2	98.1
1024	99.1	98.9	98.7	98.8
2048	100.0	100.0	100.0	100.0

Table XXII.—Temperature Coefficients.

	0° to 12°.2.		12°.2 to 25°.		25° to 35°.	
V.	Cond. units.	Per cent.	Cond. units.	Per cent.	Cond. units.	Per cent
2	2.59	2.68	2.93	2.29	3.18	1.92
8	3.35	3.00	3.45	2.27	3.94	2.01
16	3.74	3.17	3.90	2.39	4.25	1.99
32	4.04	3.24	4.17	2.40	4.48	1.97
128	4.18	2.98	4.82	2.52	5.01	1.98
512	4.78	3.24	5.19	2.53	5.44	2.00
1024	4.84	3.22	5.23	2.50	5.40	1.96
2048	4.93	3.26	5.34	2.52	5.44	1.94

Potassium Dichromate.

Table XXIII.—Molecular Conductivity.

V.	0°.	12°.6.	25°.	35°.
8	109.1	150.8	195.5	234.0
16	116.6	161.5	209.3	248.8
32	122.6	168.8	219.4	260.9
128	129.9	178.8	231.5	277.3
512	133.0	182.5	237.3	281.2
1024	133.6	185.7	240.6	287.9
2048	136.8	188.8	245.5	293.6

Table XXIV.—Percentage Dissociation.

V.	0°.	12°.6.	25°.	35°.
8	79.8	79.9	79.6	79.6
16	85.2	85.5	85.3	84.7
32	89.6	89.4	89.4	88.9
128	95.0	94.7	94.3	94.4
512	97.2	96.7	96.7	95.8
1024	97.7	98.4	98.0	98.1
2048	100.0	100.0	100.0	100.0

Table XXV.—Temperature Coefficients.

	0° to 12°.6.		12°.6 to 25°.		25° to 35°.	
V.	Cond. units.	Per cent.	Cond. units.	Per cent.	Cond. units.	Per cent.
8	3.31	3.03	3.60	2.19	3.85	1.97
16	3.56	3.05	3.85	2.38	3.95	1.89
32	3.66	2.98	4.08	2.42	4.15	1.89
128	3.88	2.99	4.25	2.38	4.39	1.90
512	3.93	2.95	4.42	2.42	4.45	1.88
1024	4.13	3.09	4.43	2.39	4.73	1.97
2048	4.13	3.02	4.57	2.42	4.81	1.96

Calcium Nitrate.

Table XXVI.—Molecular Conductivity.

V.	0°.	9°.7.	25°.	35°.
2	65.84	85.83	121.0	145.0
8	85.50	112.8	157.3	188.2
16	94.95	123.9	174.2	209.8
32	102.3	133.5	187.7	225.6
128	114.5	151.0	212.0	255.4
512	122.6	160.6	226.7	274.2
1024	125.7	164.2	235.0	282.9
2048	130.0	171.4	242.7	292.4

Table XXVII.—Percentage Dissociation.

V.	0°.	9°.7.	25°.	35°.
2	50.7	50.1	49.9	49.6
8	65.8	65.8	64.8	64.4
16	73.0	72.3	71.8	71.8
32	78.7	77.9	77.3	77.2
128	88.1	88.1	87.4	87.4
512	94.3	93.7	93.4	93.8
1024	96.7	95.8	96.8	96.8
2048	100.0	100.0	100.0	100.0

Table XXVIII.—Temperature Coefficients.

	0° to 9°.7.		9°.7 to 25°.		25° to 35°.	
V.	Cond. units.	Per cent.	Cond. units.	Per cent.	Cond. units.	Per cent.
2	2.04	3.10	2.31	2.69	2.40	1.98
8	2.81	3.29	2.91	2.58	3.09	1.96
16	2.98	3.14	3.29	2.82	3.56	2.04
32	3.22	3.15	3.54	2.62	3.79	2.02
128	3.76	3.28	3.99	2.64	4.34	2.05
512	3.92	3.19	4.32	2.69	4.75	2.10
1024	4.01	3.19	4.60	2.80	4.79	2.04
2048	4.31	3.32	4.64	2.71	4.97	2.05

Strontium Chloride.

Table XXIX.—Molecular Conductivity.

V.	0°.	9°.9.	25°.	35°.
2	81.36	106.2	141.5	172.0
8	92.97	124.3	173.7	207.4
16	101.1	134.5	187.7	225.9
32	106.3	141.5	198.4	238.7
128	118.5	157.6	225.0	271.6
512	125.0	166.1	236.7	285.4
1024	129.1	171.4	242.8	294.1
2048	133.9	176.1	248.7	300.3
4096	133.3	176.0	248.6	(303.9)

Table XXX.—Percentage Dissociation.

V.	0°.	9°.9.	25°.	35°.
2	60.8	60.3	56.9	57.3
8	69.5	70.6	69.8	69.1
16	75.5	76.4	75.5	75.2
32	79.4	80.4	79.8	79.5
128	88.5	89.5	90.5	90.5
512	93.4	94.3	95.2	95.0
1024	96.4	97.3	97.6	97.9
2048	100.0	100.0	100.0	100.0
4096	100.0	100.0	100.0	100.0

Table XXXI.—Temperature Coefficients.

	0° to 9°.9.		9°.9 to 25°.		25° to 35°.	
V.	Cond. units.	Per cent.	Cond. units.	Per cent.	Cond. units.	Per cent.
2	2.51	3.09	2.34	2.20	3.05	2.16
8	3.16	3.39	3.27	2.63	3.37	1.94
16	3.38	3.34	3.52	2.62	3.82	2.03
32	3.56	3.35	3.90	2.76	4.03	2.03
128	3.96	3.34	4.46	2.83	4.66	2.07
512	4.15	3.32	4.67	2.81	4.87	2.06
1024	4.27	3.31	4.73	2.76	5.13	2.11
2048	4.27	3.22	4.81	2.73	5.16	2.07
4096	4.31	3.23	4.81	2.73	5.31	2.14

Strontium Nitrate.

Table XXXII.—Molecular Conductivity.

V.	0°.	10°.	25°.	35°.
2	63.24	81.25	112.4	135.4
8	84.33	112.8	154.1	181.7
16	93.33	124.8	171.4	205.7
32	100.7	133.3	185.3	223.5
128	114.8	151.4	211.2	254.0
512	122.5	161.6	227.1	273.5
1024	126.9	167.0	233.7	282.3
2048	131.3	171.9	238.6	287.5

Table XXXIII.—Percentage Dissociation.

V.	0°.	10°.	25°.	35°.
2	48.2	47.3	47.1	47.1
8	64.2	65.5	64.6	63.2
16	71.1	72.6	71.8	71.5
32	77.7	77.5	77.7	77.7
128	87.4	88.1	88.5	88.4
512	93.3	94.0	95.2	95.1
1024	96.7	97.2	97.9	98.2
2048	100.0	100.0	100.0	100.0

Table XXXIV.—Temperature Coefficients.

	0° to 10°.		10° to 25°.		25° to 35°.	
V.	Cond. units.	Per cent.	Cond. units.	Per cent.	Cond. units.	Per cent.
2	1.80	2.85	2.07	2.55	2.30	2.05
8	2.85	3.38	2.75	2.44	2.76	1.79
16	3.14	3.36	3.11	2.49	3.43	2.00
32	3.26	3.24	3.47	2.60	3.82	2.06
128	3.66	3.19	3.99	2.63	4.28	2.03
512	3.91	3.19	4.37	2.70	4.64	2.04
1024	4.01	3.16	4.45	2.66	4.86	2.08
2048	4.06	3.10	4.45	2.59	4.89	2.05

Strontium Formate.

Table XXXV.—Molecular Conductivity.

V.	0°.	15°.5.	25°.	35°.
2	48.82	73.05	89.25	107.9
8	69.86	105.2	130.0	157.9
16	77.61	119.1	147.9	178.6
32	85.69	129.9	160.7	195.8
128	99.57	147.9	184.0	225.0
512	105.0	153.5	193.4	237.7
1024	109.0	168.6	209.0	254.1
2048	111.8	172.2	212.5	258.1

Table XXXVI.—Percentage Dissociation.

V.	0°.	15°.5.	25°.	35°.
2	43.7	42.4	42.0	41.8
8	62.5	61.1	61.2	61.1
16	69.4	69.0	69.6	69.2
32	76.6	75.4	75.6	75.9
128	89.1	85.9	86.6	87.2
512	93.9	89.2	91.0	92.1
1024	97.5	97.9	98.3	98.5
2048	100.0	100.0	100.0	100.0

Table XXXVII.—Temperature Coefficients.

	0° to 15°.5.		15°.5 to 25°.		25° to 35°.	
V.	Cond. units	Per cent.	Cond. units.	Per cent.	Cond. units.	Per cent.
2	1.56	3.20	1.70	2.32	1.87	2.09
8	2.27	3.25	2.61	2.48	2.77	2.13
16	2.67	3.44	3.03	2.54	3.07	2.08
32	2.85	3.32	3.24	2.49	3.51	2.18
128	3.11	3.13	3.80	2.57	4.10	2.23
512	3.13	2.98	4.12	2.68	4.43	2.29
1024	3.84	3.52	4.25	2.52	4.49	2.24
2048	3.91	3.49	4.24	2.46	4.56	2.14

Barium Bromide.

Table XXXVIII.—Molecular Conductivity.

V.	0°.	10°.	25°.	35°.
2	91.81	119.3	158.6	188.1
8	103.4	137.0	187.4	224.0
16	109.3	144.8	198.9	238.8
32	114.4	151.0	209.4	251.4
128	123.6	163.7	228.5	274.4
512	131.8	175.5	246.8	298.2
1024	133.8	177.2	249.9	301.6
2048	134.2	178.7	252.6	305.7

Table XXXIX.—Percentage Dissociation.

V.	0°.	10°.	25°.	35°.
2	68.4	66.8	62.8	61.5
8	77.1	76.7	74.2	73.3
16	81.5	81.0	78.7	78.1
32	85.3	84.5	82.9	82.2
128	92.1	91.6	90.5	89.8
512	98.2	98.2	97.7	97.6
1024	99.7	99.2	98.9	98.7
2048	100.0	100.0	100.0	100.0

Table XL.—Temperature Coefficients.

	0° to 10°.		10° to 25°.		25° to 35°.	
V.	Cond. units.	Per cent.	Cond. units.	Per cent.	Cond. units.	Per cent.
2	2.74	2.98	2.62	2.20	2.95	1.86
8	3.36	3.25	3.36	2.45	3.66	1.95
16	3.55	3.25	3.60	2.49	3.99	2.01
32	3.66	3.20	3.89	2.58	4.20	2.01
128	4.01	3.24	4.32	2.64	4.59	2.01
512	4.37	3.32	4.75	2.71	5.14	2.08
1024	4.34	3.24	4.85	2.74	5.18	2.07
2048	4.45	3.32	4.93	2.76	5.24	2.07

Barium Nitrate.

Table XLI.—Molecular Conductivity.

V.	0°.	10°.	25°.	35°.
8	76.37	103.0	146.4	177.3
16	88.29	117.6	165.2	200.1
32	97.62	129.8	183.2	219.8
128	114.4	150.8	210.0	251.8
512	124.3	163.8	229.2	275.2
1024	127.4	167.8	234.2	281.6
2048	131.4	171.6	239.8	288.8

Table XLII.—Percentage Dissociation.

V.	0°.	10°.	25°.	35°.
8	58.1	60.0	61.1	61.4
16	67.2	68.5	68.9	69.3
32	74.3	75.6	76.4	76.1
128	87.1	87.9	87.6	87.2
512	94.6	95.5	95.6	95.3
1024	97.0	97.8	97.7	97.5
2048	100.0	100.0	100.0	100.0

Table XLIII.—Temperature Coefficients.

	0° to 10°.		10° to 25°.		25° to 35°.	
V.	Cond. units.	Per cent.	Cond. units.	Per cent.	Cond units.	Per cent.
8	2.66	3.48	2.89	2.81	3.09	2.11
16	2.93	3.32	3.17	2.70	3.49	2.11
32	3.22	3.30	3.56	2.74	3.66	2.00
128	3.64	3.18	3.95	2.62	4.18	1.99
512	3.95	3.18	4.36	2.66	4.60	2.01
1024	4.04	3.17	4.43	2.64	4.74	2.02
2048	4.02	3.06	4.55	2.65	4.90	2.04

Barium Formate.

Table XLIV.—Molecular Conductivity.

V.	0°.	10°.	25°.	35°.
2	51.67	67.74	93.97	112.1
8	72.22	95.34	133.4	159.2
16	77.72	102.7	144.6	173.8
32	85.56	114.3	160.6	193.1
128	86.20	114.3	162.4	197.4
512	102.2	133.6	182.0	215.2
1024	103.0	135.0	184.0	226.2
2048	111.8	149.4	210.0	257.6

Table XLV.—Percentage Dissociation.

V.	0°.	10°.	25°.	35°.
2	46.2	45.3	44.8	43.5
8	64.6	63.8	63.5	61.8
16	69.5	68.7	68.9	69.0
32	76.5	76.5	76.5	75.0
128	77.1	76.5	77.3	76.6
512	91.4	89.4	86.7	83.5
1024	92.1	90.3	87.7	87.8
2048	100.0	100.0	100.0	100.0

Table XLVI.—Temperature Coefficients.

	0° to 10°.		10° to 25°.		25° to 35°.	
V.	Cond. units.	Per cent.	Cond. units.	Per cent.	Cond. units.	Per cent.
2	1.60	3.10	1.75	2.58	1.81	1.93
8	2.31	3.20	2.54	2.66	2.58	1.93
16	2.49	3.20	2.79	2.72	2.92	2.02
32	2.87	3.35	3.09	2.70	3.25	2.02
128	2.81	3.26	3.27	2.86	3.50	2.16
512	3.15	3.08	3.23	2.41	3.32	1.82
1024	3.20	3.10	3.33	2.46	4.22	2.29
2048	3.76	3.36	4.04	2.70	4.76	2.27

Barium Acetate.

Table XLVII.—Molecular Conductivity.

V.	0°.	10°.	25°.	35°.
2	40.16	53.25	76.18	89.95
8	59.05	79.46	113.3	136.0
16	65.68	87.10	124.3	149.3
32	72.93	97.58	139.5	168.6
128	78.15	104.5	149.0	181.2
512	90.75	123.1	176.9	215.8
1024	92.63	124.7	180.5	219.8
2048	95.96	129.3	186.3	226.7

Table XLVIII.—Percentage Dissociation.

V.	0°.	10°.	25°.	35°.
2	41.9	41.2	40.9	39.7
8	63.0	61.5	60.8	60.0
16	68.4	67.4	66.7	66.0
32	76.0	75.5	74.9	74.4
128	81.4	80.8	80.0	79.9
512	94.6	95.2	95.0	95.2
1024	96.5	96.4	96.9	97.0
2048	100.0	100.0	100.0	100.0

Table XLIX.—Temperature Coefficients.

	0° to 10°.		10° to 25°.		25° to 35°.	
V.	Cond. units.	Per cent.	Cond. units	Per cent.	Cond. units.	Per cent.
2	1.30	3.24	1.52	2.85	1.37	1.80
8	2.04	3.45	2.26	2.84	2.27	2.00
16	2.14	3.26	2.48	2.85	2.52	2.03
32	2.46	3.38	2.79	2.86	2.91	2.09
128	3.63	3.37	2.97	2.84	3.22	2.16
512	3.23	3.06	3.59	2.91	3.89	2.20
1024	3.20	3.45	3.72	2.98	3.93	2.18
2048	3.33	3.47	3.80	2.93	4.04	2.17

Magnesium Sulphate.

Table L.—Molecular Conductivity.

V.	0°.	10°.	25°.	35°.
2	32.12	43.14	60.57	72.68
8	45.70	60.90	85.62	102.4
16	50.95	68.14	96.50	115.0
32	59.57	79.73	112.4	135.3
128	71.17	95.38	135.9	164.4
512	95.57	128.3	183.3	221.9
1024	102.7	138.4	198.3	240.9
2048	111.1	148.5	215.2	261.0

Table LI.—Percentage Dissociation.

V.	0°.	10°.	25°.	35°.
2	28.9	29.1	28.2	27.8
8	41.1	41.0	39.8	39.2
16	45.9	45.9	44.8	44.1
32	53.6	53.7	52.2	51.8
128	64.1	64.2	63.2	63.0
512	86.0	84.4	85.2	85.0
1024	92.4	93.2	92.3	92.3
2048	100.0	100.0	100.0	100.0

Table LII.—Temperature Coefficients.

	0° to 10°.		10° to 25°.		25° to 35°.	
V.	Cond. units.	Per cent.	Cond. units.	Per cent.	Cond. units.	Per cent.
2	1.10	3.42	1.16	2.69	1.21	2.00
8	1.52	3.33	1.65	2.71	1.67	1.95
16	1.71	3.36	1.89	2.77	1.85	1.92
32	2.01	3.37	2.18	2.73	2.29	2.04
128	2.42	3.40	2.75	2.88	2.85	2.10
512	3.27	3.42	3.73	2.91	3.86	2.11
1024	3.57	3.48	3.99	2.88	4.26	2.15
2048	3.74	3.37	4.45	2.99	4.58	2.22

Cupric Bromide.

Table LIII.—Molecular Conductivity.

V.	0°.	13°.3.	25°.	35°.
2	75.27	103.9	135.3	156.1
8	91.31	131.0	169.6	203.8
16	99.30	141.4	183.0	220.3
32	105.0	149.8	194.3	234.1
128	118.2	169.0	220.0	266.0
512	122.2	177.3	230.8	278.4
1024	125.4	181.2	236.6	285.9
2048	131.4	187.5	242.7	295.0
4096	...	...	248.8	300.2
8192	...	...	274.8	325.1

Table LIV.—Percentage Dissociation.

V.	0°.	13°.3.	25°.	35°.
2	57.3	55.4	55.7	52.9
8	69.5	69.9	69.9	69.1
16	75.6	75.4	75.4	74.7
32	79.9	79.9	80.1	79.3
128	90.0	90.1	90.6	90.2
512	93.0	94.6	95.1	94.4
1024	95.4	96.6	97.5	96.9
2048	100.0	100.0	100.0	100.0

Table LV.—Temperature Coefficients.

	0° to 13°.3.		13°.3 to 25°.		25° to 35°.	
V.	**Cond. units.**	**Per cent.**	**Cond. units.**	**Per cent.**	**Cond. units.**	**Per cent.**
2	2.16	2.87	2.68	2.58	2.08	1.54
8	2.99	3.27	3.30	2.51	3.42	2.02
16	3.17	3.19	3.50	2.48	3.73	2.04
32	3.37	3.21	3.75	2.50	3.98	2.04
128	3.82	3.23	4.35	2.57	4.60	2.09
512	4.14	3.38	4.37	2.57	4.76	2.06
1024	4.19	3.34	4.73	2.61	4.93	2.08
2048	4.22	3.21	4.72	2.52	5.23	2.15
4096	..	..	..	..	5.14	..
8192	..	..	..	..	5.03	..

Chromium Chloride.

Table LVI.—Molecular Conductivity.

V.	0°.	10°.	25°.	35°.
8	116.3	153.7	216.9	261.7
16	128.7	171.1	243.0	294.5
32	137.5	184.2	262.9	319.9
128	152.6	204.5	297.0	365.3
512	190.6	260.8	384.0	475.4
1024	204.9	280.5	420.5	522.8
2048	214.6	294.3	441.7	553.4

Table LVII.—Percentage Dissociation.

V.	0°.	10°.	25°.	35°.
8	54.2	52.2	49.1	47.3
16	60.0	58.1	55.0	53.2
32	64.1	62.6	59.5	57.8
128	71.1	69.5	67.2	66.0
512	88.8	88.6	86.9	85.9
1024	95.5	95.3	95.2	94.5
2048	100.0	100.0	100.0	100.0

Table LVIII.—Temperature Coefficients.

	0° to 10°.		10° to 25°.		25° to 35°.	
V.	Cond. units.	Per cent.	Cond. units.	Per cent.	Cond. units.	Per cent.
8	3.74	3.30	4.21	2.74	4.48	2.07
16	4.24	3.29	4.79	2.80	5.15	2.12
32	4.67	3.40	5.25	2.85	5.70	2.17
128	5.19	3.40	6.17	3.35	6.83	2.29
512	7.02	3.68	8.21	3.15	9.14	2.30
1024	7.56	3.69	9.33	3.33	10.23	2.43
2048	7.97	3.71	9.83	3.34	11.17	2.53

Chromium Nitrate.

Table LIX.—Molecular Conductivity.

V.	0°.	10°.	25°.	35°.
2	87.17	112.1	154.7	183.6
8	117.6	153.1	214.0	256.5
16	129.7	169.7	238.8	287.4
32	138.5	181.9	258.1	312.6
128	149.0	198.9	286.2	350.7
512	188.7	253.0	370.2	459.4
1024	203.0	274.0	412.9	511.8
2048	210.4	295.3	438.0	550.9

Table LX.—Percentage Dissociation.

V.	0°.	10°.	25°.	35°.
2	41.4	38.0	35.3	33.3
8	55.9	51.9	48.9	46.6
16	61.6	57.5	54.5	52.2
32	65.8	61.8	58.9	56.8
128	70.8	67.4	65.3	63.7
512	89.7	85.7	84.5	83.6
1024	96.5	92.8	94.3	93.4
2048	100.0	100.0	100.0	100.0

Table LXI.—Temperature Coefficients.

	0° to 10°.		10° to 25°.		25° to 35°.	
V.	Cond. units.	Per cent.	Cond. units.	Per cent.	Cond. units.	Per cent.
2	2.49	2.86	2.84	2.53	2.89	1.87
8	3.55	3.02	4.06	2.65	4.25	1.99
16	4.00	3.08	4.61	2.72	4.86	2.04
32	4.34	3.13	5.08	2.79	5.45	2.11
128	4.99	3.35	5.82	2.93	6.45	2.25
512	6.43	3.41	7.81	3.09	8.92	2.41
1024	7.10	3.50	9.26	3.38	9.89	2.40
2048	8.49	4.04	9.51	3.22	11.29	2.58

Ferric Chloride.

Table LXII.—Molecular Conductivity.

V.	0°.	10°.	25°.	35°.
2	80.50	104.6	143.6	169.9
8	127.2	168.5	238.1	285.4
16	143.4	190.7	274.6	332.7
32	166.7	226.0	328.3	400.4
128	198.9	274.0	401.9	508.9
512	351.2	563.1	707.2	945.0
1024	486.3	688.4	892.4	1130.3
2048	609.7	799.9	1028.2	1235.6

Table LXIII.—Temperature Coefficients.

	0° to 10°.		10° to 25°.		25° to 35°.	
V.	Cond. units.	Per cent.	Cond. units.	Per cent.	Cond. units.	Per cent.
2	2.41	2.99	2.60	2.49	2.65	1.85
8	4.13	3.25	4.64	2.75	4.73	1.99
16	4.73	3.30	5.59	2.93	5.81	2.12
32	5.93	3.56	6.82	3.02	7.21	2.20
128	7.51	3.78	8.53	3.11	10.70	2.66
512	21.1	6.01	9.61	1.71	23.78	3.36
1024	20.2	4.15	13.66	1.98	23.60	2.64
2048	19.0	3.12	12.27	1.50	24.16	2.35

Ferric Nitrate.

Table LXIV.—Molecular Conductivity.

V.	0°.	10°.	25°.	35°.
2	97.68	128.1	181.6	220.7
8	138.2	185.7	266.5	328.2
16	150.7	202.7	295.3	364.3
32	171.4	233.7	342.6	422.6
128	199.5	271.7	399.4	491.4
512	371.3	408.7	705.7	927.0
1024	490.9	571.4	877.7	1116.5
2048	585.2	693.5	961.6	1183.0

Table LXV.—Temperature Coefficients.

	0° to 10°.		10° to 25°.		25° to 35°.	
V.	Cond. units.	Per cent.	Cond. units.	Per cent.	Cond. units.	Per cent.
2	3.04	3.12	3.57	2.79	3.91	2.15
8	4.75	3.44	5.39	2.90	6.17	2.32
16	5.20	3.44	6.17	3.04	6.90	2.34
32	6.23	3.63	7.26	3.11	8.00	2.34
128	7.22	3.62	8.50	3.13	9.20	2.30
512	3.74	1.01	19.80	4.84	22.13	3.14
1024	8.05	1.64	20.42	3.57	23.88	2.72
2048	10.83	1.85	18.61	2.68	22.14	2.30

Nickel Sulphate.

Table LXVI.—Molecular Conductivity.

V.	0°.	10°.	25°.	35°.
2	28.77	38.37	54.58	64.38
8	40.38	54.42	77.06	90.95
16	47.78	64.00	90.44	106.9
32	54.78	73.23	103.5	123.0
128	73.95	99.92	140.3	168.4
512	93.12	124.7	177.5	213.5
1024	100.4	134.8	193.8	234.6
2048	108.3	145.5	208.7	253.9

Table LXVII.—Percentage Dissociation.

V.	0°.	10°.	25°.	35°.
2	26.6	25.8	26.2	25.4
8	37.5	37.4	36.9	35.8
16	44.1	44.0	43.3	42.1
32	50.6	50.3	49.6	48.5
128	68.3	68.7	67.2	66.3
512	86.0	85.7	85.1	84.1
1024	92.7	92.6	92.9	92.4
2048	100.0	100.0	100.0	100.0

Table LXVIII.—Temperature Coefficients.

	0° to 10°.		10° to 25°.		25° to 35°.	
V.	Cond. units.	Per cent.	Cond. units.	Per cent.	Cond. units.	Per cent.
2	0.96	3.34	1.08	2.81	0.98	1.80
8	1.38	3.40	1.50	2.75	1.39	1.80
16	1.62	3.39	1.76	2.75	1.64	1.81
32	1.84	3.36	2.01	2.74	1.95	1.88
128	2.59	3.50	2.69	2.69	2.81	2.00
512	3.16	3.39	3.52	2.82	3.60	2.03
1024	3.44	3.43	3.93	2.91	4.08	2.11
2048	3.72	3.43	4.21	2.89	4.52	2.17

Nickel Acetate.

Table LXIX.—Molecular Conductivity.

V.	0°.	10°.	25°.	35°.
2	20.11	27.24	39.22	47.46
8	38.95	52.07	74.10	89.29
16	47.81	64.03	91.60	110.2
32	54.11	73.82	105.8	128.1
128	69.22	92.82	134.6	164.0
512	76.66	103.5	150.7	184.7
1024	78.65	105.9	153.9	189.1
2048	82.24	110.9	160.6	196.6

Table LXX.—Percentage Dissociation.

V.	0°.	10°.	25°.	35°.
2	24.5	24.6	24.4	24.1
8	47.4	47.0	45.1	45.4
16	56.8	57.7	57.0	56.1
32	65.8	66.6	65.9	65.2
128	84.2	83.7	83.8	83.4
512	93.2	93.3	93.8	93.9
1024	95.6	95.5	95.8	96.2
2048	100.0	100.0	100.0	100.0

Table LXXI.—Temperature Coefficients.

	0° to 10°.		10° to 25°.		25° to 35°.	
V.	Cond. units.	Per cent.	Cond. units.	Per cent.	Cond. units.	Per cent.
2	0.71	3.53	0.79	2.90	0.82	2.09
8	1.31	3.39	1.47	2.82	1.51	2.04
16	1.62	3.39	1.84	2.87	1.86	2.03
32	1.97	3.64	2.13	2.89	2.23	2.11
128	2.36	3.41	2.78	3.00	2.94	2.18
512	2.68	3.50	3.14	3.03	3.40	2.26
1024	2.72	3.46	3.20	3.02	3.52	2.29
2048	2.86	3.48	3.31	2.98	3.60	2.24

Cobalt Sulphate.

Table LXXII.—Molecular Conductivity.

V.	0°.	10°.	25°.	35°.
2	29.47	39.22	55.10	65.57
8	42.06	56.00	78.37	93.14
16	49.26	65.61	91.97	109.4
32	56.26	75.04	105.4	125.8
128	75.89	101.5	143.4	172.1
512	94.88	126.9	180.2	218.1
1024	101.9	137.6	196.9	239.2
2048	110.9	148.4	214.1	259.2

Table LXXIII.—Percentage Dissociation.

V.	0°.	10°.	25°.	35°.
2	26.6	26.4	25.7	25.3
8	37.9	37.7	36.6	35.9
16	44.4	44.2	43.0	42.2
32	50.7	50.6	49.2	48.5
128	68.4	68.4	67.0	66.4
512	85.6	85.5	84.2	84.2
1024	91.9	92.7	92.0	92.3
2048	100.0	100.0	100.0	100.0

Table LXXIV.—Temperature Coefficients.

	0° to 10°.		10° to 25°.		25° to 35°.	
V.	Cond. units.	Per cent.	Cond. units.	Per cent.	Cond. units.	Per cent.
2	0.97	3.29	1.06	2.70	1.04	1.89
8	1.39	3.30	1.49	2.66	1.47	1.88
16	1.63	3.31	1.76	2.68	1.74	1.89
32	1.88	3.34	2.02	2.69	2.04	1.94
128	2.56	3.37	2.79	2.75	2.87	2.00
512	3.21	3.38	3.55	2.79	3.79	2.10
1024	3.57	3.50	3.95	2.87	4.23	2.15
2048	3.75	3.38	4.38	2.95	4.51	2.11

Cobalt Acetate.

Table LXXV.—Molecular Conductivity.

V.	0°.	10°.	25°.	35°.
2	22.20	29.79	42.55	51.02
8	41.31	55.27	78.37	94.00
16	50.07	67.20	95.68	114.9
32	56.92	76.66	109.8	132.1
128	71.25	95.67	136.8	166.3
512	78.29	106.0	153.6	188.1
1024	78.88	107.1	155.3	189.8
2048	82.71	113.2	163.7	199.3

Table LXXVI.—Percentage Dissociation.

V.	0°.	10°.	25°.	35°.
2	26.8	26.3	26.0	25.6
8	50.0	48.8	47.9	46.1
16	60.5	59.4	58.5	57.7
32	68.8	67.7	67.1	66.3
128	86.1	84.5	83.6	83.4
512	94.7	93.6	93.8	94.4
1024	95.4	94.6	94.9	95.2
2048	100.0	100.0	100.0	100.0

Table LXXVII.—Temperature Coefficients.

	0° to 10°.		10° to 25°.		25° to 35°.	
V.	Cond. units.	Per cent.	Cond. units.	Per cent.	Cond. units.	Per cent.
2	0.75	3.37	0.85	2.85	0.87	2.04
8	1.39	3.36	1.54	2.79	1.56	1.99
16	1.71	3.42	1.90	2.83	1.92	2.01
32	1.97	3.46	2.21	2.88	2.23	2.03
128	2.44	3.42	2.74	2.86	2.95	2.16
512	2.77	3.54	3.15	2.97	3.45	2.25
1024	2.82	3.58	3.21	2.99	3.45	2.22
2048	3.05	3.69	3.37	2.98	3.56	2.17

Lead Nitrate.

Table LXXVIII.—Molecular Conductivity.

V.	0°.	10°.	25°.	35°.
2	46.30	63.55	92.68	113.0
8	71.12	97.32	139.8	169.5
16	84.43	103.3	161.5	195.6
32	93.85	128.3	181.5	118.8
128	115.1	153.1	214.0	256.7
512	129.1	171.9	238.3	287.1
1024	133.6	178.1	247.4	297.5
2048	135.1	178.7	247.2	299.0

Table LXXIX.—Percentage Dissociation.

V.	0°.	10°.	25°.	35°.
2	34.3	35.6	37.5	37.8
8	52.6	54.5	55.3	56.7
16	62.5	63.4	65.3	65.4
32	69.5	71.8	73.4	73.2
128	85.2	85.7	86.6	85.9
512	95.6	96.2	96.4	96.0
1024	98.9	99.7	100.0	99.5
2048	100.0	100.0	100.0	100.0

Table LXXX.—Temperature Coefficients.

	0° to 10°.		10° to 25°.		25° to 35°.	
V.	Cond. units.	Per cent.	Cond. units.	Per cent.	Cond. units.	Per cent.
2	1.72	3.71	1.94	3.05	2.03	2.19
8	2.62	3.68	2.83	2.91	2.97	2.12
16	2.88	3.41	3.21	2.83	3.41	2.11
32	3.44	3.67	3.55	2.77	3.73	2.05
128	3.80	3.30	4.06	2.65	4.27	2.00
512	4.28	3.32	4.43	2.58	4.88	2.05
1024	4.45	3.33	4.62	2.59	5.01	2.03
2048	4.36	3.23	4.57	2.55	5.18	2.10

Trichloracetic Acid.

Table LXXXI.—Molecular Conductivity.

V.	0°.	10°.	25°.	35°.
2	161.3	198.8	250.1	279.7
8	194.0	241.6	305.3	346.5
16	204.6	252.6	320.6	363.8
32	210.5	260.2	332.4	377.8
128	215.5	268.4	343.5	391.3
512	221.2	275.5	350.7	400.2
1024	220.3	272.6	350.4	399.3
2048	217.4	272.9	347.0	396.7

Table LXXXII.—Percentage Dissociation.

V.	0°.	10°.	25°.	35°.
2	72.9	72.2	71.3	69.9
8	87.7	87.7	87.1	86.6
16	92.5	91.7	91.4	90.9
32	95.5	94.5	94.8	94.4
128	97.4	97.4	97.9	97.8
512	100.0	100.0	100.0	100.0
1024	100.0	100.0	100.0	100.0
2048	100.0	100.0	100.0	100.0

Table LXXXIII.—Temperature Coefficients.

	0° to 10°.		10° to 25°.		25° to 35°.	
V.	Cond. units.	Per cent.	Cond. units.	Per cent.	Cond. units.	Per cent.
2	3.75	2.32	3.42	1.72	2.96	1.18
8	4.76	2.45	4.25	1.76	4.12	1.35
16	4.80	2.35	4.53	1.79	4.32	1.35
32	4.97	2.36	4.81	1.85	4.54	1.37
128	5.29	2.45	5.00	1.86	4.78	1.39
512	5.43	2.45	5.01	1.82	4.95	1.41
1024	5.23	2.37	5.24	1.92	4.89	1.40
2048	5.55	2.55	4.94	1.81	4.97	1.43

Racemic Acid.

Table LXXXIV.—Molecular Conductivity.

V.	0°.	15°.	25°.	35°.
2	8.77	12.60	15.19	17.54
8	17.87	25.70	30.89	35.65
16	24.72	35.64	42.89	49.46
32	34.04	49.17	59.02	68.18
128	62.32	90.59	108.4	124.8
512	109.0	155.0	184.4	212.5
1024	134.7	190.0	220.6	247.3
2048	169.5	238.3	290.9	336.7

Table LXXXV.—Percentage Dissociation.

V.	0°.	15°.	25°.	35°.
2	4.23	4.32	4.27	4.26
8	6.61	8.80	8.68	8.65
16	11.9	12.2	12.1	12.0
32	16.4	16.8	16.6	16.6
128	30.2	31.0	30.5	30.3
512	52.5	53.1	51.8	51.6
1024	64.9	65.1	62.0	60.0
2048	81.7	81.6	81.7	81.7

Table LXXXVI.—Temperature Coefficients.

	0° to 15°.		15° to 25°.		25° to 35°.	
V.	Cond. units.	Per cent.	Cond. units.	Per cent.	Cond. units.	Per cent.
2	0.26	2.91	0.26	2.06	0.24	1.55
8	0.52	2.92	0.52	2.02	0.48	1.54
16	0.73	2.94	0.73	2.03	0.66	1.53
32	1.01	2.97	0.99	2.00	0.92	1.55
128	1.88	3.02	1.78	1.97	1.64	1.51
512	3.07	2.82	2.94	1.89	2.81	1.52
1024	3.69	2.74	3.06	1.61	2.67	1.21
2048	4.39	2.71	5.26	2.21	4.58	1.57

Picric Acid.

Table LXXXVII.—Molecular Conductivity.

V.	0°.	15°.	25°.	35°.
32	193.0	260.2	303.7	345.1
128	201.1	272.4	319.9	365.2
512	207.6	280.9	329.6	377.5
1024	206.9	281.7	332.6	379.9
2048	203.5	277.1	325.6	372.7

Table LXXXVIII.—Percentage Dissociation.

V.	0°.	15°.	25°.	35°.
32	93.0	92.4	91.3	90.8
128	96.9	96.7	96.2	96.1
512	100.0	99.7	99.1	99.4
1024	100.0	100.0	100.0	100.0
2048	100.0	100.0	100.0	100.0

Table LXXXIX.—Temperature Coefficients.

	0° to 15°.		15° to 25°.		25° to 35°.	
V.	Cond. units.	Per cent.	Cond. units.	Per cent.	Cond. units.	Per cent.
32	4.48	2.32	4.35	1.67	4.14	1.36
128	4.75	2.36	4.75	1.77	4.53	1.42
512	4.89	2.36	4.87	1.73	4.79	1.42
1024	4.99	2.41	4.89	1.74	4.93	1.48
2048	4.73	2.30	4.85	1.75	4.71	1.45

Propionic Acid.

Table XC.—Molecular Conductivity.

V.	0°.	15°.	25°.	35°.
2	1.06	1.49	1.74	1.98
8	2.31	3.19	3.72	4.22
16	3.26	4.51	5.29	5.99
32	4.65	6.42	7.52	8.49
128	9.09	12.53	14.78	16.69
512	17.18	23.45	27.39	30.70
1024	23.49	32.09	37.58	42.29
2048	31.51	42.88	51.04	36.80

Table XCI.—Percentage Dissociation.

V.	0°.	15°.	25°.	35°.
2	0.48	0.49	0.49	0.49
8	1.04	1.06	1.04	1.06
16	1.47	1.50	1.47	1.50
32	2.10	2.12	2.09	2.13
128	4.10	4.15	4.12	4.18
512	7.74	7.77	7.63	7.69
1024	10.6	10.6	10.5	10.6
2048	14.2	14.2	14.2	14.2

Table XCII.—Temperature Coefficients.

	0° to 15°.		15° to 25°.		25° to 35°.	
V.	Cond. units.	Per cent.	Cond. units.	Per cent.	Cond. units.	Per cent.
2	0.03	2.64	0.03	1.68	0.02	1.32
8	0.05	2.25	0.05	1.66	0.05	1.31
16	0.08	2.55	0.08	1.70	0.07	1.32
32	0.12	2.54	0.11	1.71	0.08	1.29
128	0.23	2.52	0.23	1.80	0.19	1.29
512	0.42	2.43	0.39	1.68	0.33	1.21
1024	0.57	2.43	0.55	1.71	0.47	1.25
2048	0.76	2.41	0.82	1.90	0.58	1.13

o-Nitrobenzoic Acid.

Table XCIII.—Molecular Conductivity.

V.	0°.	15°.	25°.	35°.
32	98.15	120.5	132.2	140.6
128	146.9	184.9	205.6	222.6
512	187.5	244.1	278.3	307.8
1024	196.3	261.7	301.8	336.9
2048	200.8	267.4	312.2	351.8

Table XCIV.—Percentage Dissociation.

V.	0°.	15°.	25°.	35°.
32	43.1	39.6	37.2	35.2
128	64.4	60.8	57.9	55.7
512	82.2	80.3	78.4	77.0
1024	86.1	86.1	85.0	84.2
2048	88.1	88.0	88.0	88.0

Table XCV.—Temperature Coefficients.

	0° to 15°.		15° to 25°.		25° to 35°.	
V.	Cond. units.	Per cent.	Cond. units.	Per cent.	Cond. units.	Per cent.
32	1.49	1.52	1.17	0.97	0.84	0.59
128	2.53	1.72	2.07	1.12	1.70	0.76
512	3.77	2.61	3.42	1.40	2.95	1.06
1024	4.36	2.22	4.01	1.53	3.51	1.16
2048	4.44	2.21	4.48	1.68	3.96	1.27

m-Nitrobenzoic Acid.

Table XCVI.—Molecular Conductivity.

V.	0°.	15°.	25°.	35°.
128	40.10	56.85	67.66	77.56
512	71.95	101.0	120.0	137.1
1024	92.44	129.8	153.8	175.4
2048	115.1	160.7	190.5	216.7

Table XCVII.—Percentage Dissociation.

V.	0°.	15°.	25°.	35°.
128	18.7	19.0	19.1	19.2
512	33.6	33.8	33.8	33.9
1024	43.1	43.4	43.3	43.4
2048	53.7	53.8	53.7	53.6

Table XCVIII.—Temperature Coefficients.

	0° to 15°.		15° to 25°.		25° to 35°.	
V.	Cond. units.	Per cent.	Cond. units.	Per cent.	Cond. units.	Per cent.
128	1.12	2.79	1.08	1.90	0.99	1.46
512	1.87	2.60	1.90	1.88	1.71	1.43
1024	2.49	2.69	2.40	1.85	2.16	1.40
2048	3.04	2.64	2.98	1.85	2.62	1.38

Discussion of Results.

We have already shown that widely different conclusions have been reached regarding the effect of temperature on the conductivity and ionization of electrolytes in aqueous solution.

For the purpose of arriving at something definite it was desirable to extend the work to as many different compounds as possible. The present investigation includes twenty-eight inorganic salts and six organic acids. The salts were so chosen as to have a wide range of physical and chemical properties, especially those of valence and the power of salts to crystallize with water of crystallization.

By glancing at any one of the preceding tables it will be seen that the molecular conductivity of electrolytes increases with rise in temperature from 0° to 35°; that conductivity increases with increase in dilution up to a certain maximum value, and that dissociation increases with increase in dilution up to the point where the electrolyte is completely dissociated. These facts are, however, so well established by previous work that additional evidence seems almost unnecessary.

A maximum in the conductivity curve, as described by Sack,[1] Kohlrausch,[2] Noyes,[3] and others, was not observed at any time during the progress of the work. This, however, was not to be expected, since a maximum conductivity generally occurs at much higher temperatures than those at which we worked.

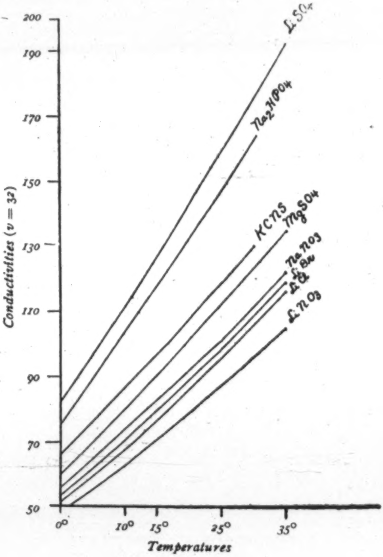

Fig. III.

With these preliminary observations we shall turn to the real questions at issue. In the first place: Is conductivity a linear function of the temperature? As is pointed out in the introduction, different conclusions have been reached by different experimenters. Our work goes to show that, except in the case of water, *conductivity is not a linear function of the temperature at any dilution with which we worked.* The increase in conductivity with rise in temperature is greater

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[1] Wied. Ann., **43**, 212 (1891).

[2] Pogg. Ann., **154**, 215 (1875).

[3] J. Am. Chem. Soc., **26**, 134 (1904).

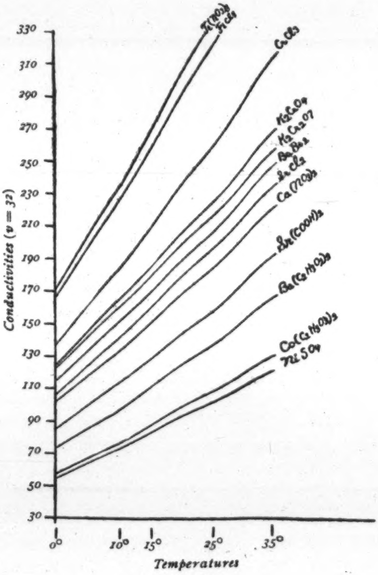

Fig. IV.

the higher the temperature. This becomes more apparent by observing the curves in Figs. III, IV, and V, where molecular conductivities are the ordinates and temperatures the abcissae. Water presents the only exception to this rule. In Fig. II the conductivity of water has been plotted against temperature, and as is seen the relation is a linear one from 0° to 35°.

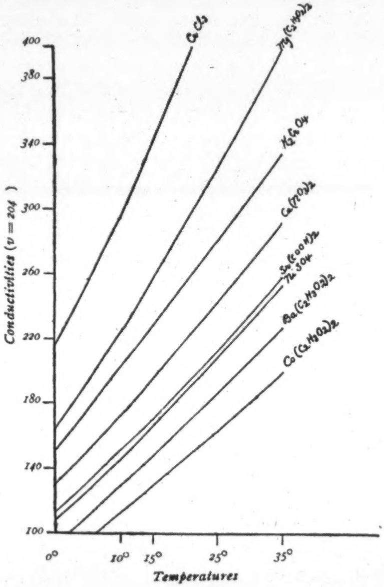

Fig. V.

The increase in the conductivity of electrolytes with rise in temperature is undoubtedly due, as has been pointed out by Jones,[1] largely to the fact that all electrolytes in aqueous solution are hydrated to a greater or less extent, and that rise in temperature diminishes the extent of this hydration. It is clear that when the ions become partly or wholly freed from the water attached to them, their mass, and probably their size, will be reduced. This will allow them to move through the solution with less friction and, consequently, increase the conductivity. Therefore, it is fair to conclude that the conductivity of those ions which are hydrated to the greatest

[1] THIS JOURNAL, **35**, 445 (1905).

extent in solution would be most affected by change in temperature. All of the experimental data, here given, support this conclusion.

In Table XCIX. is given a list of the substances investigated. They are arranged in the order of their increasing temperature coefficients. By referring to these tables it will be seen that those substances with little or no hydrating power are at the top, while those possessing a marked hydrating power appear towards the bottom of the list. Upon this hypothesis we may explain the fact that the change in conductivity with temperature is not a linear function in the case of ordinary electrolytes, while in the case of water it is a linear function.

Table XCIX.

Substance.	Temp. Coef., 0°–10°. $V = 2048$.	Temp. Coef., 25°–35°. $V = 2048$.
Lithium nitrate	1.76	2.07
Lithium chloride	1.92	2.31
Lithium bromide	1.94	2.34
Sodium nitrate	2.27	2.44
Potassium sulphocyanate	2.24	2.72
Nickel acetate	2.86	3.60
Cobalt acetate	3.03	3.56
Cobalt sulphate	3.75	4.51
Nickel sulphate	3.72	4.52
Barium acetate	3.33	4.04
Strontium formate	3.91	4.56
Disodium phosphate	3.68	4.44
Barium formate	3.76	4.76
Magnesium sulphate	3.74	4.58
Lithium sulphate	3.77	4.85
Potassium dichromate	4.13	4.81
Potassium chromate	4.93	5.44
Calcium nitrate	4.31	4.97
Strontium chloride	4.31	5.31
Cupric bromide	4.22	5.23
Barium bromide	4.45	5.24
Barium nitrate	4.02	4.90
Strontium nitrate	4.06	4.89
Lead nitrate	4.36	5.18
Chromium chloride	7.97	11.17
Chromium nitrate	8.49	11.29
Ferric nitrate	10.83	22.14
Ferric chloride	19.00	24.16

As has just been pointed out, the electrolytes whose ions are hydrated in solution will show a large increase in conductivity with rise in temperature. This is equivalent to saying that their conductivities are parabolic functions of the temperature. In the case of water it is difficult to see how the hydrogen or hydroxyl ions could become appreciably hydrated; and the fact that the conductivity of water increases regularly with rise in temperature goes to show that no such hydration exists, but that the increase in conductivity is conditioned chiefly by a change in the viscosity of the medium. This latter phenomenon we know to be a linear one with respect to temperature, and by *a priori* reasoning we would conclude that the conductivity of water, or of any entirely unhydrated electrolyte, if such existed, would also be a linear function of the temperature. Facts and theory are in perfect accord on this point.

Another factor, playing an important rôle in conductivity work, is hydrolysis. Scarcely too great emphasis can be laid on the fact that water is decomposed in the presence of a large number of substances in solution, and yet it is surprising to see how much conductivity work has been done where this fact has been overlooked or disregarded.

To ascertain the effect of hydrolysis on the conductivity of strongly hydrolyzed salts, we have included iron and chromium compounds in this work. By referring to the tables where the molecular conductivities of these compounds are given, it is seen that the increase in their conductivities at high dilutions is so abnormally large that one might think nothing but gross experimental error could account for it. It is also seen that their conductivities are disproportionately larger at higher temperatures. These results plainly show that hydrolysis is enormously increased with rise in temperature. Now the question arises: Is hydrolysis manifested only by salts of strong acids and weak bases, and *vice versa*, or where both acid and base are weak; or is it a phenomenon common to all electrolytes? The latter view is the one held by Ciamician,[1] Euler,[2] Bauer,[3] and others. In order to obtain evidence on this point let us again turn to the preceding tables. It is seen that in nearly every case the conductivity changes more or less suddenly from $V = 1024$ to $V = 2048$. The conductivity is by no means a constant at those dilutions, yet in the majority of cases the substances are thought to be completely dissociated. For these reasons we are convinced that nearly all, if not all, electrolytes are hydrolyzed in dilute solution.

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[1] Z. physik. Chem., **6**, 403 (1890).

[2] *Ibid.*, **21**, 257 (1896).

[3] *Ibid.*, **23**, 409 (1897).

Granting this fact, how would it affect the percentage dissociation as calculated by the formula: μ_v/μ_∞? It is clear that if hydrolysis takes place at high dilutions the value of μ_∞ as found is too large by that amount. For this reason α becomes smaller than it otherwise would. It is a well-known fact that hydrolysis is greatly accelerated by rise in temperature, and, consequently, the values for μ_∞ will grow proportionately larger as the temperature is raised. This will, of course, diminish the calculated value of the dissociation more and more the higher the temperature.

The above reasoning is based on the assumption that hydrolysis takes place to a greater extent in dilute than in more concentrated solutions. In case of weakly hydrolyzed compounds we should say that this is the case, for mass action then comes into play; whereas, with strongly hydrolyzed salts like the iron, lead, and aluminium compounds, the effect of hydrolysis would probably be more pronounced before high dilutions are reached. Referring to the tables of the iron salts we see that this theory is supported by the facts.

A summary of the results of the effect of rise in temperature on dissociation is given in Table C.

It is seen that the results are of the same general character as those obtained by Jones and West.[1] The fact that an increase in dissociation with rise in temperature is found with the iron salts, lead nitrate, and *m*-nitrobenzoic acid is doubtless due to hydrolysis, as is explained above.

For the reasons already mentioned it seems to us that the true effect of temperature on dissociation cannot be rigidly ascertained unless hydration, on the one hand, and hydrolysis,

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[1] This Journal, **34**, 357 (1905).

Table C.

α decreases with rise in temperature.

Potassium sulphocyanate
Barium bromide
"   formate
Sodium nitrate
Disodium phosphate
Lithium nitrate
"   chloride
"   bromide
"   sulphate
Calcium nitrate
Strontium formate
Magnesium sulphate
Nickel   "
Cobalt   "
Chromium chloride
"   nitrate
Trichloracetic acid
Picric acid
o-Nitrobenzoic acid

α increases with rise in temperature.

Ferric chloride
"   nitrate
Lead nitrate
m-Nitrobenzoic acid

α independent of temperature.

Potassium chromate
Potassium dichromate
Cupric bromide
Racemic acid
Propionic acid

α decreases in concentrated, but increases in dilute solutions.

Barium acetate
Cobalt   "
Nickel   "

α increases slightly in dilute solutions.

Strontium chloride
"   nitrate
Barium   "

on the other, are taken into account. It is a fact, however, that many electrolytes are affected only to a relatively small extent by these influences, and that the value for dissociation calculated without taking these into account is not far from the correct value.

When we examine the temperature coefficients expressed in conductivity units, we find that, without exception, they increase as dilution increases, and for every salt they increase with rise in temperature; but the organic acids, on the other hand, have decreasing temperature coefficients with rise in temperature. This is more clearly seen by reference to Fig. 6, where coefficients are the ordinates and temperatures the abscissae.

The temperature coefficients expressed in percentages, on the other hand, invariably decrease with rise in temperature. The fact that temperature coefficients of all salts increase with rise in temperature, whereas both organic and inorganic acids have decreasing temperature coefficients, is easily explained by the hydrate theory of Jones. The metallic cations are probably the ones that are chiefly hydrated in solution, and when the temperature is raised this hydration is diminished, thus greatly increasing the ionic mobility, while no such increase is possible where metallic ions are absent.

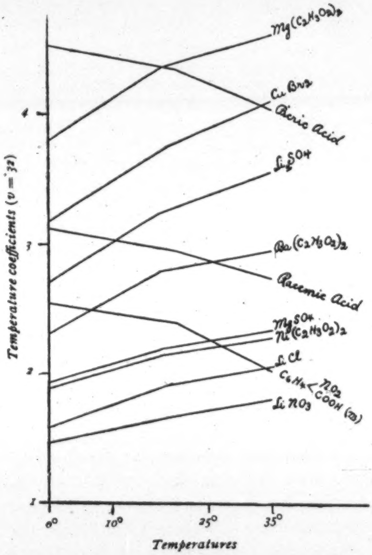

Fig. VI.

During the progress of this work we noticed a striking phenomenon in the telephone that should be mentioned. A short time after the circuit was closed, thus allowing the current to pass through the cell containing the electrolyte, a sudden increase in the loudness of the tone was noticed when the key was held near the node on the bridge. This phenomenon was at first thought to be due to polarization, but later, when the same effect could be obtained with any solution, even with redistilled water, and since no noticeable change in conductivity could be detected as a result of it, we concluded that this phenomenon is novel in character, and as far as we know has not been described before. The time for this loudness to come on varied from a few seconds to eight or ten minutes, depending upon the nature of the electrolyte.

It is futile to speculate what might be its cause until more experimental evidence is obtained. One suggestion that might have an element of truth in it is the following: The kinetic vibrations of the ions may be influenced by the electrical stress, set up within the solution, in such a way that they will be brought to take place in the direction of the lines of force present. This idea could be illustrated by the molecular arrangement thought to exist in a permanent magnet.

Conclusions.

The following points have been verified or established by the present work:

1. The molecular conductivity of electrolytes in aqueous solution increases as a parabolic function of the temperature from 0° to 35°.
2. Conductivity increases with increase in dilution.
3. With increase in dilution dissociation increases up to a maximum value where it is complete.
4. Hydrolysis is a formidable source of error in obtaining the true value for μ_∞ and, consequently, in obtaining the true dissociation.
5. Disregarding the effect of hydrolysis, dissociation decreases with rise in temperature.
6. The conductivity of water is a linear function of the temperature.
7. Salts that are strongly hydrated in solution show a greater increase in conductivity with rise in temperature than the salts that are slightly hydrated.
8. The temperature coefficients, expressed in conductivity units, increase with rise in temperature. Those of the organic acids are exceptions.

9. The temperature coefficients expressed in percentages decrease with rise in temperature.

10. The temperature coefficients of compounds with similar properties vary in a similar manner with change in temperature.

We are extending, in this laboratory, this investigation to all of the more common electrolytes, organic and inorganic. We are studying the temperature coefficients of conductivity and of dissociation over the range of temperatures extending from 35° to as near the boiling points of the solutions as it is possible to go.

PHYSICAL CHEMICAL LABORATORY,
JOHNS HOPKINS UNIV.,
May, 1908.

REVIEWS.

A TREATISE ON CHEMISTRY. By H. E. ROSCOE, F.R.S., and C. SCHORLEMMER, F.R.S. Vol II.—THE METALS. London: Macmillan and Co. 1907. pp. 1436. Price, $7.50.

The treatise of Roscoe and Schorlemmer has always been regarded as the most reliable, and, all things considered, the most satisfactory treatise on chemistry. The last edition, Vol. II., appeared in 1897. In regard to this, the fourth edition, Sir Henry Roscoe says: "Much new and important matter with regard to the Metals and their Compounds has come to light in the ten years since the last edition of this work appeared, and in the present volume care has been taken to include all the more important points connected with the recent discoveries."

The earlier editions are so well and so favorably known that general comment is uncalled for. A fairly complete examination of this new edition shows that it embodies the important later discoveries, including those in the field of physical chemistry. Whether the book is sufficiently saturated with the modern physical conceptions is a question that can be answered only by physical chemists. Extremists will perhaps feel that the authors have not gone far enough into the ionic field.

The attitude of the authors towards the later developments appears to be appreciative and fair. Take, for example, this passage referring to the corpuscular theory of the constitution of the atom: "This theory is admirably adapted to explain the phenomena of electrolysis and all reactions which occur between ions, as well as all cases of combination between electro-positive and electro-negative elements. Considerable difficulties, however, arise when it is applied to elements which are not markedly electro-positive or electro-negative, and especially to those compounds in which a number of the atoms of the same element are combined together. In such a simple compound as ethane, CH_3–CH_3, for instance, it is necessary to suppose that one of the carbon atoms acts as the positive and the other as the negative element, although no difference between the two has been recognized chemically. Similar considerations hold with regard to the molecules of the elements themselves, many of which are composed of two atoms of the element united together.

"These difficulties have not yet been entirely surmounted, although attempts have been made to devise a consistent empirical system which will be in accordance with these electrochemical requirements, by supposing that each element possesses a definite and limited power of combining both with relatively positive and with negative elements."

The chapter dealing with the "Metals of the Rare Earths" will be especially welcome, as it no doubt is the best summary of the work on this subject. In regard to the group dysprosium, holmium, erbium, and thulium, the authors say: "The terbia originally isolated from crude yttria by Mosander subsequently received the name of *erbia* (Berlin), and has been shown by Soret, Cleve, Thalén, and Lecoq de Boisbaudran to consist of at least four earths, the true *erbia*, *holmia*, *thulia*, and *dysprosia*. The salts of all these show absorption bands, but it is doubtful if any one of the four, with the possible exception of dysprosium, is an individual substance. Erbium forms a rose-colored oxide and salts of the same color, which in solution show absorption bands, while the salts of dysprosium are green or yellow."

In regard to ytterbium they say: "Doubts as to the individuality of the ytterbium compounds have been expressed by Auer von Welsbach."

The subject of "The Radioactive Elements" is dealt with in twenty-eight pages in a very clear way. The recent very remarkable results obtained by Cameron and Ramsay on the formation of lithium salts from copper salts by the action of radium emanation are included. The chapter concludes with these words: "The atom must now be regarded as an aggregate of simpler forms of matter, possessing enormous potential energy. This aggregate may, under conditions which we are not yet able to control, break down into simpler forms, a large amount of energy being evolved in the change. Hence the unalterability of the atom postulated by Dalton must be modified, and the atom must be regarded as a complex, but of a higher order than the chemical compounds formed by the union of atoms with each other." It is impossible at present to establish a more precise characterization of this higher order of complex substances than is expressed in the statement that the decomposition of an atom is beyond our control and that the energy changes are of a higher order of magnitude than is the case with ordinary compounds.

"These discoveries, however, while opening out new views as to the constitution of matter, are in no degree inconsistent with the well-established facts of chemical combination or with the application of them to Dalton's atomic theory."

Taking this book all in all, it can be spoken of only in the highest terms. It ought to be in every chemical library, whether that library is large or small. I. R.

SPECTRUM ANALYSIS. By JOHN LANDAUER. Second Edition. Rewritten by J. BISHOP TINGLE, PH.D., F.C.S. New York: John Wiley & Sons. 1907.

This book is an enlarged and rewritten translation of the German original which first appeared in 1898. Its purpose may, perhaps, best be stated by quoting the words of the translator in his "Preface to the Second Edition." He says, "In judging it (*i. e.*, this book) regard should be had to its object. It does not pretend to be an exhaustive work on the subject, but merely an elementary guide to those who, with relatively little knowledge of physics, desire to understand something of the general scope and methods of spectrum analysis and to make practical use of the spectroscope;......" The book begins with an historical review of the science of spectroscopy and a bibliography of works on spectrum analysis. This is followed by chapters dealing with the following subjects: Physical Properties of Light, Spectroscopes, Spectroscopic Instruments for Special Purposes, Spectroscopic Adjuncts, Spectra, Spectra of the Elements, Absorption Spectra, Solar Spectrum, Other Celestial Bodies.

Altogether, the book serves very well as an introduction to spectrum analysis. The main fault which might be found with it is that, in some respects, it is not sufficiently modern. This criticism applies mainly to the absence of a treatment of the spectroscopic analysis of complexes—a subject which, in the estimate of the reviewer, ought to form a most important part of the book. The two fundamental arguments which are at the basis of the entire science of spectrum analysis are, (1) that each element produces a spectrum which is absolutely characteristic, (2) that the spectroscope is capable of detecting the existence of elements which are present in quantities much too minute for chemical analysis. The first essential to a practical application of spectrum analysis is an intimate knowledge of the characteristic appearance of the spectra of the elements—and it must be admitted that, in the present volume, this part of the subject is well treated. Not only is the descriptive part well done, but the wave lengths of the principal lines, determined by numerous observers who have based their determinations upon various standards, have all been recalculated so as to be in accord with Rowland's values. In addition, the complete list of Rowland's determinations of the wave lengths of the Fraunhofer lines (extending from λ 3000 to 7714 A. V.) is given.

The principal shortcomings of the book are to be found in the treatment of the subject-matter coming under the second argument previously referred to. The problem which most often confronts the spectroscopist is the analysis of a complex such as a bit of rock or meteorite, or a mixture of unknown gases. Now it is a well-known fact that, in the spectrum of a complex of elements, certain elements obliterate more or less completely the spectrum of the others, even though the latter be present in relatively large quantities. In recent years considerable attention has been paid to this matter. Methods have been developed for bringing out the easily marked spectra, and the wave lengths of those lines which are most liable to persist have been determined—thus making possible the detection of those elements which would otherwise remain undiscovered. The fact that the great majority of books on spectrum analysis devote but little space to this most important branch of the subject would make its discussion in a modern treatise highly desirable.

A careful perusal of the book has yielded but few misprints or misstatements, and as those which have been found do not materially influence the usefulness of the text, there is not much need of pointing out these slight defects individually. Considering the book as a whole, it well fulfils the purpose for which it was written and ought to be of great service to chemists.

A. H. PFUND.

A LABORATORY OUTLINE FOR DETERMINATIONS IN QUANTITATIVE CHEMICAL ANALYSIS. By ALBERT F. GILMAN, S.B., A.M., Professor of Chemistry, Ripon College, Ripon, Wisconsin, Easton, Pa.: Chemical Publishing Co. 1908. pp. 88.

This little book is intended to be used as a combined laboratory guide and record book of experiments performed by students just beginning work in quantitative analysis. The more common methods of determining the metals and some of the acids are given. The rather meagre directions are supplemented at the end of each determination by references to Fresenius and Classen and by questions concerning details of the method of procedure. The directions are in general clear, although the English could in many cases be improved. C. A. R.

UEBER DIE SCHICHTUNGEN BEI DIFFUSION. Eine Voruntersuchung von Raphael Ed. Liesegang. Düsseldorf. 1907. pp. 66.

This little pamphlet records a number of interesting and probably important observations, in reference to the layers that are formed in various processes of diffusion, especially into gelatine. A number of beautiful plates are given, showing the various layers that were observed. H. C. J.